A QUANTITATIVE ANALYSIS OF KAMATIVI'S WATER QUALITY

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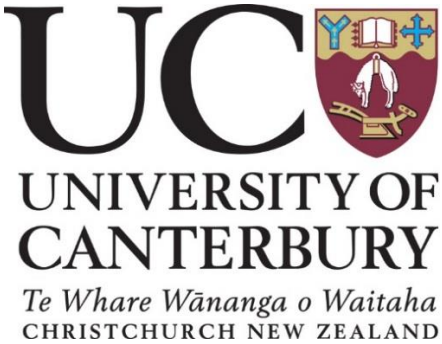

ABSTRACT

Kamativi is a tin-mining town in north-western Zimbabwe, in Hwange district of Matabeleland north province. The population of the town, and its peripheries, is an estimated 7,000 people, most of whom are former miners, laid off from work following closure of the mine in 1994. Mining operations ran for about 58 years prior to then, before low tin prices at the time forced indefinite suspension of business. The Hwange Rural District Council (HRDC) subsequently took over the administration of the town from the Zimbabwe Mining Development Company (ZMDC). This takeover included the running of the town's water supply system which uses surface abstraction from a local dam to supply its reticulated system. The mine was the main source of economic income in the area so its closure led to deterioration of everything in Kamativi, and water problems have dogged the town ever since. Prompted by media reports about poor water quality, and availability problems cited by residents, this research was undertaken into the physico-chemical and microbiological characteristics of Kamativi's water supply, and how it compares to Zimbabwean drinking water standards and guidelines. The purpose was to determine the impact, if any, of mining and other anthropogenic activities on the quality of water in Kamativi, and to suggest a way to improve or resolve Kamativi's water quality issues. Samples from different water sources in Kamativi were collected during part of the wet and dry seasons in 2016. Arsenic concentrations exceed the Zimbabwe and World Health Organization's health-based guidelines for drinking, in five out of six main sources, including tap water. Two other water sources had concentrations of aluminium and manganese that exceeded the standards on at least one occasion. The distribution of trace metal concentrations by geographic location of the water bodies suggests that proximity to the mine influences the concentration of trace metal pollutants. Faecal contamination was evident in raw water, as indicated by the presence of *E. coli* and faecal coliforms. It was concluded that the water did not meet the standards for drinking water and needs treatment. It was also determined that the mine has an impact on the water quality and there is a risk of arsenic toxicity. A recommendation was made that Kamativi reintroduces full water treatment and treats for trace metals, particularly arsenic. Ongoing monitoring and evaluation is also needed to gauge improvements, lessen pollution, and prevent future impacts. Further research is required to determine the source and speciation of arsenic within the mining area and to predictively assess impacts of the proposed reopening of the mine on the local water supply system.

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1.0 INTRODUCTION

1.1 Water as a developmental issue

Water is a basic human need recognized by the World Health Organization (WHO) and the United Nations Children's Fund (UNICEF) as a critical part of the Millennium Development Goals (MDGs) (UNICEF and WHO, 2012) and their successor, the Sustainable Development Goals (SDGs) (UNICEF and WHO, 2015). Water is the focal point of SDG Goal 6 on clean water and sanitation and is closely linked to other goals regarding health, poverty, and climate change. In March 2012, the United Nations (UN), in its review report on progress on drinking water and sanitation, announced that it had met its target of reducing by half the proportion of people with no access to safe drinking water, in advance of its 2015 deadline (UNICEF and WHO, 2012). However, in the same report, the statistics show that at least 11% of the global population, that is, over 783 million people are still without access to safe drinking water, and about 2.5 billion are without sanitation facilities. Only 63% have improved sanitation access since the enactment of MDGs. This tends to have a direct negative impact on water quality due to environmental pollution problems (UNICEF and WHO, 2012). In the 2015 issue of the progress report, the UN stated that widespread water scarcity, poor water quality as well as inadequate sanitation are negatively impacting food security, livelihood and educational opportunities for the poor across many parts of world.

Water availability and quality are critical for a potable water supply system. In developed countries, the quality of all public drinking water is regularly monitored and the data obtained has an influence on the policy of water supply for municipalities and other responsible authorities. UNICEF and WHO in 2012 warned that adequate scientific measurement of water quality is not possible globally. The MDG target of safe drinking water was measured by gathering country-by-country data on the use of improved drinking water sources, which is not always an accurate way of assessing the safety of water sources, since it does not measure the effectiveness of different procedures employed in individual countries (UNICEF and WHO, 2012). The Zimbabwean town of Kamativi, for example, with its dilapidated reticulated water system, would be considered to have access to safe drinking water due to the classification of its method of delivery, yet the quality of the water is unknown due to the lack of ongoing monitoring and quality control. Over 40% of all people globally who lack

access to safe drinking water live in sub-Saharan Africa (UNICEF and WHO, 2012).

1.2 Water management in Zimbabwe

Zimbabwe, with a land area of 390,757 km² and a population estimate of 13.5 million (ZimStat, 2013), is a developing country in Southern Africa. Zimbabwe is a landlocked country, bordered to its north-west by Zambia and Mozambique on the north-east, South Africa to the south, and Botswana on its south-west (Figure 1.1).

Figure 1.1 Location of Zimbabwe in the African continent (Google maps, 2015).

Zimbabwe inherited a fairly well developed urban water system and a largely undeveloped rural system at independence in 1980, due to colonial policies in the past which had little

regard for the mostly native populated rural areas (Water and Sanitation Program (WSP), 2011). A lot has changed since then, however, with about 80% of the country, inclusive of urban areas, having improved water delivery methods, according to the Water, Sanitation and Hygiene report published by UNICEF, in 2012. Nonetheless, the subject of water quality is still a highlight of significant disparities that exist between major urban centres and the rest of the country. For example, there is little to no water infrastructural development in some populated rural areas in the Lowveld (WSP, 2011). This seems to result from many factors, including management failures in local government structures and the economic downturn that the country has been going through since the early 2000s (Munangagwa, 2009).

The national water management structure puts municipalities in charge of urban water supply while central government branches and rural residents are the main stakeholders of rural water resources (Figure 1.2). The Ministry of Water Resources and Development (MWRD) is the arm of central government responsible for water resources management outside major towns and cities (Zimbabwe Water Act, 1998). Its main technical functions are carried out by a parastatal organization under its wings, the Zimbabwe National Water Authority (ZINWA) which is further divided into seven catchment-based management units, officially termed "catchment councils" as illustrated in Figure 1.2 (ZINWA Act, 1998). Responsibilities and functions are not always concise and in some rural areas there is no direct practical responsibility (Manzungu and Mabiza, 2004).

Despite bureaucracy and little direct public participation, challenges, and deficiencies of water resources in Zimbabwe urban areas are well known and documented, while monitoring in rural areas is not well practised and residents there are considered as stakeholders in their own right, along with government (Manzungu and Mabiza, 2004).

In some rural villages, boreholes and protected wells have been sunk either by the government or with the support of non-governmental organizations (NGOs) to provide safe drinking water for villagers (WSP, 2011). In the most remote rural areas however, water provision is so underdeveloped that each household or homestead normally makes its own means of procurement, often from unprotected sources or hand dug wells. Quality monitoring is rare in rural areas and the main reason given by the Ministry of Water and Resource Development (MWRD) is lack of adequate financial resources (WSP, 2011). The Environmental Management Agency (EMA) which falls under the Ministry for the

Environment and Climate, monitors ambient water quality for environmental pollution (EMA, 2002)

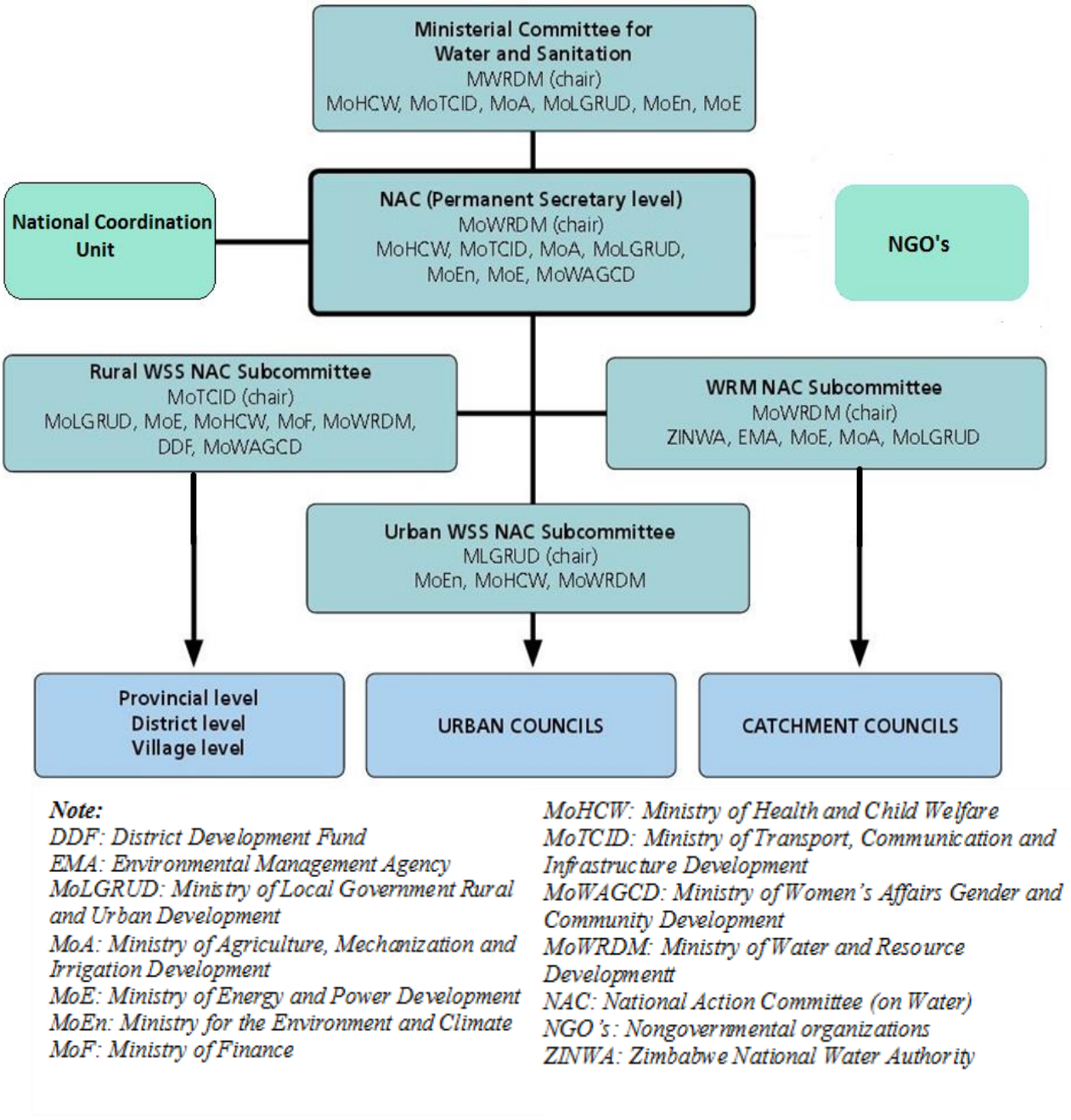

Figure 1.2 National water management structure of Zimbabwe (ZINWA, 2002; WSP, 2011)

1.2.1 Infrastructural decay

From early 2002 to 2010, more than 60% of the water provision infrastructure in rural Zimbabwe was reported as being in a state of disrepair and believed to provide unsafe water which ordinarily requires decontamination or other forms of treatment (WSP, 2011). Despite a brief resurgence between 2010 and 2013, the economic outlook in Zimbabwe as of 2016 is still bleak and has slowed or halted infrastructural recovery programmes (African Economic Outlook, 2016). In urban areas, sporadic reticulated water supply is the norm with instances of poor quality on the rise since the early 2000s (Manzungu and Mabiza, 2004). Neglected communities, such as former mining towns and informal settlements, also suffer the same fate of poor water provision. Freshwater resources in Zimbabwe have an uneven distribution related to microclimatic conditions, physical geography and level of development. The level of development on one hand is heavily affected by availability of meaningful economic interest that can attract investment in a particular area. Sadly, most of Zimbabwe's public infrastructure was built in the 1960s to 1980s, and renewal or maintenance has not always been fast or effective enough, especially outside main urban centres (Ashton et al, 2001). Reticulation pipes in the capital, Harare, for instance, were only rehabilitated as late as 2014 after many years of water losses due to leakages from damaged and aged water pipes.

There have been some positive developments, however, such as the recent completion of Tokwe-Mukosi dam, 18 years after construction began, with a total cost of nearly US$260 million (Maponga, 2017). This dam, with a capacity of 1.8 billion cubic metres, is intended to provide water for an arid region in the southern part of Zimbabwe's Masvingo province (Maponga, 2017).

1.2.2 Geographical setup

As articulated by Statutory Instrument 33 of 2000, Zimbabwe has seven catchment areas namely Mazowe, Runde, Manyame, Gwayi Catchment (includes Hwange District where Kamativi is located), Mzingwane, Save and Sanyati catchments (ZINWA Act, 1998). These are shown on a map in Figure 1.3.

There is significant variability in rainfall patterns in different parts of Zimbabwe. The eastern end of the country is on a higher topographical level and generally tends to receive more rainfall and has a more temperate climate. The same goes for Harare which sits at 1500 m

above sea level. The situation, however, is different in a section of the country known as the Lower Veld, where rainfall is lower and the climate hotter. Cyclical changes occur every now and again, placing higher demands on water in areas where is not easily accessible in sufficient quantities. There are often competing priorities as far as water provision goes, and the funds available are often directed to the cause that is capable of generating more income for either a private organization involved or even a government department. However, under the Zimbabwe Water Act, ZINWA is the ultimate custodian of water resources belonging to the public.

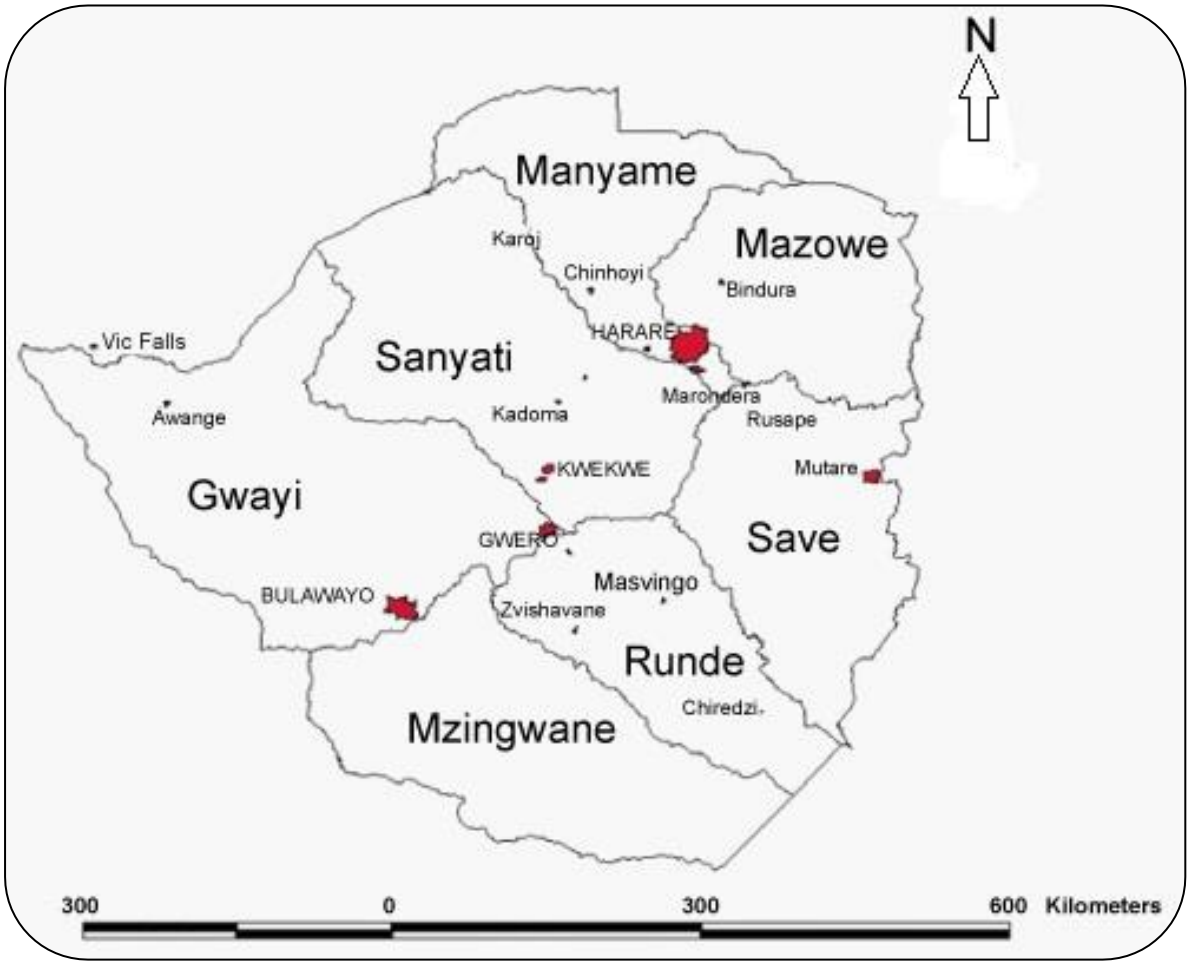

Figure 1.3 The seven water catchments in Zimbabwe. The town of Kamativi lies under Hwange District to the north-west of the country [Source: Chikodzi, D. (2013)].

Scarcity of water has been worsened in most cases by the economic decline that Zimbabwe has gone through over the last two to three decades. The flocking of people from rural areas towards urban centres in search of work and subsistence opportunities such as vending has put a strain on water resources. This, in turn, has lessened the effectiveness of the system in many urban areas (Mweembe and Munkuli, 2009). Small mining towns in Zimbabwe

historically tend to have a unique trend whereby the corporate organization that is responsible for mineral exploitation will normally be the one that takes responsibility for most municipal duties, including water provision (Mweembe and Munkuli, 2009).

Problems posed by scarce water supplies in other urban areas were therefore not usually an issue for mining towns, especially when the business was booming. The contamination of the environment and, in the process, water supplies has been an issue in Zimbabwe, however, and more so prior to the passing of the Environmental Management Act of 2002.

1.2.3 Mining and water resources in Zimbabwe

Mining is a major economic activity in Zimbabwe and has been so for many years since the 1890s when the first European settlers colonized the country, mostly for territorial and mineral benefits. As such, the development of many urban centres, big and small, in Zimbabwe had a link to mining as an economic driver (Kamete, 2012).

In recorded history, mining activities fuelled urban development and breathed economic life into areas where mines were established and as such prosperity ensued. However, mining is a fickle activity; deposits of minerals sometimes run out in an area or the demand for them may diminish. In some cases, mere mismanagement has prevented mining regions from being self-sustaining, resulting in natural resource utilisation not only failing to bring tangible development for the common people, but also causing a great deal of harm to the environment (Kamete, 2012). This environmental damage often includes potentially harmful impacts to water resources or human health.

With mine closure or a decline in economic output comes the unwanted side effect of unsustainable urban settlements sometimes far from other towns and with very limited connectivity or alternative livelihoods. Poverty and ghost towns have emerged under such a regime. Lack of a continuity plan for a post-mine period for towns that develop as mining areas is probably the biggest planning mistake that authorities involved in awarding mining concessions in Zimbabwe have made in the past (Kamete, 2012).

Mining has a significant impact on the environmental water quality and necessitates a more advanced system of water supply management than those usually available in rural areas. Rural areas tend to host almost all new mines.

The current legislation, in the form of the EMA act has taken the side effects of mining into account but only as from 2002, after many mines had operated and some even closed without any environmental impact assessment (EIA) being carried out. In recent years, the EMA has made it mandatory for mining entities to follow certain standards regarding effluent or other impacts to the environment, which inevitably include freshwater systems. Past pollution effects are therefore still evident in most mining areas, potentially affecting places where potable water is obtained. An exacerbating factor is that rural people often fetch water directly from rivers or natural lakes and just boil it prior to consumption. Mines are known to leach harmful trace elements, and therefore there is a high likelihood of people drinking from a contaminated water source in the proximity of mining areas.

1.3 The tin mining process and its effect on water

Mineral resource extraction is normally done in progressive and sometimes recurrent stages that may have a negative impact on the environment and freshwater resources. The extents to which this is likely to happen depend largely on the process involved, proactive research into potential side effects, and available mitigation measures.

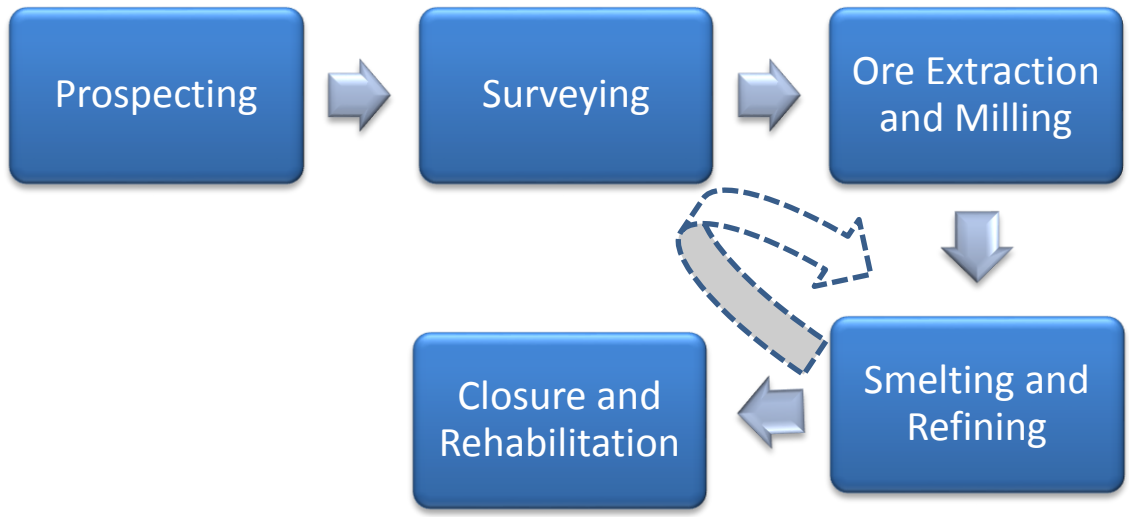

Figure 1.4 General mining progressions, with the dashed arrow showing the recovery/ recycling process (Tin Research Institute (ITRI), 2012)

During the prospecting stage, experienced or knowledgeable geologists look for indicators in an area of the existence of minerals being sought. This may include physical observation of land, water, and sediment. In most cases, it can involve sampling, which may continue

through the stage of surveying a quantity of deposits after the existence of precious minerals has been confirmed. These are planning stages that, under present legislation in Zimbabwe, must only proceed when a comprehensive EIA has been done and approved, to minimise unwanted effects on the environment (EMA, 2002).

It is usually at the onset of the ore extraction stage that the real conflict between mining and the environment begins. Clearing of expanses of land and vegetation, followed by the setting up of structures and machinery can easily upset the balance of that particular ecosystem. River systems can be dammed, blocked or diverted to make mining possible. In milling, smelting and refining, chemicals may be used whose disposal may be detrimental to environmental water quality if sufficient mitigation measures are not taken. Elevated concentrations of heavy metals and other pollutants have been found in water bodies near various local mines in Southern Africa including Zimbabwe (Ashton et al, 2001). In the years prior to 2002, many mines including Kamativi tin Mine in Zimbabwe have closed either under the pretext of reopening soon or under indefinite circumstances, with the last process of rehabilitation not necessarily fulfilled to the standard that is required to ensure the safety of communities around the mining area (Kamete, 2012).

Different mineral-procurement processes have different procedures that have their own respective impacts on environments in which mining operations take place. Some of the most commonly used methods in Zimbabwe include opencast mining (also known as quarrying), underground mining (shallow and deep), strip mining, riverine alluvial mining (both wet and dry) and small scale mining (panning). Due to the wide availability of alluvial minerals in some rural communities, small scale mining or panning is very common in Zimbabwe and has been proposed by some jobless ex-miners in Kamativi (R. Phiri, personal communication, 18 April 2016). It is also very destructive to the environment and poses a real threat of pollution to water resources.

1.3.1 During tin mining

Tin (Sn) is mined for its wide use in coating steel containers, making soldering material, as part of dental amalgams, electrical connections, and so on (ITRI, 2012). It is found as a mineral in the ore cassiterite (SnO_2), which is relatively insoluble in its raw form. According to the International Tin Research Institute (ITRI, 2012), tin ore is obtained in two different ways, depending on the ore deposits and landscape: either by hard-rock mining or alluvial mining. The release of potential pollutants from the cassiterite happens mainly at the

processing stage where separation of the tin element from the parent rock occurs. Levels of retention of by-product metals may vary depending on the technology used, as well as the level of recovery deemed operationally viable by an individual mining entity. By-product metals such as tantalum, niobium, lithium, and tungsten are common in the tin ore (ITRI, 2012; ZMDC, n.d)

Hard-rock mining

In this method, cassiterite and other ore mineral boulders are broken out of the rock by drilling through them or using blasting equipment in the case of large rock faces. The broken rock is then transferred to a concentrator which crushes and grinds the material before concentrating it, usually by gravity. Following this stage, a technique known as flotation may be used to improve the amount of pulverised tin recovery or to recover tin from ore residues. Process flows may also have a provision for recovery of other by-product metals, which include lithium and tantalum.

Alluvial mining

Alluvial tin mining is popular in situations where the ore already exists in a sedimentary state as a result of natural rock weathering or river erosion. In the period prior to the mid-1980s, the usual method of extracting larger tin alluvium was by bucket ladder dredging. The alluvial ore is excavated and moved along by a chain mechanism of buckets to the inside of the dredge. Here it is washed and concentrated, more or less similarly to the method above. In some cases, smaller cutter-suction dredges are employed; these move more easily and tend to yield a better grade concentrate. An example of this is in South-east Asia where mines with smaller deposits and those that are unsuitable for dredging (e.g., due a very rough bedrock) are driven by gravel pumping. The alluvial ore is broken down by a high-pressure water jet, forming slurry which is, in turn, pumped into the concentrating plant (ITRI, 2012).

Smelting and refining

Tin smelting is essentially the chemical reduction of tin oxide ($SnO_{2)}$ by heating with carbon to produce tin metal and carbon dioxide gas:

$$SnO_2 + C + \text{heat} \rightarrow Sn + CO_2\ (+\text{slag}) \qquad \text{(eqn 1)}$$

Retreatment of the slag is usually necessary in order to obtain sufficient recovery levels of the metals smelted (ITRI, 2012; ZMDC, n.d.). An example of a complete process in a tin mine would be as shown in Figure 1.5.

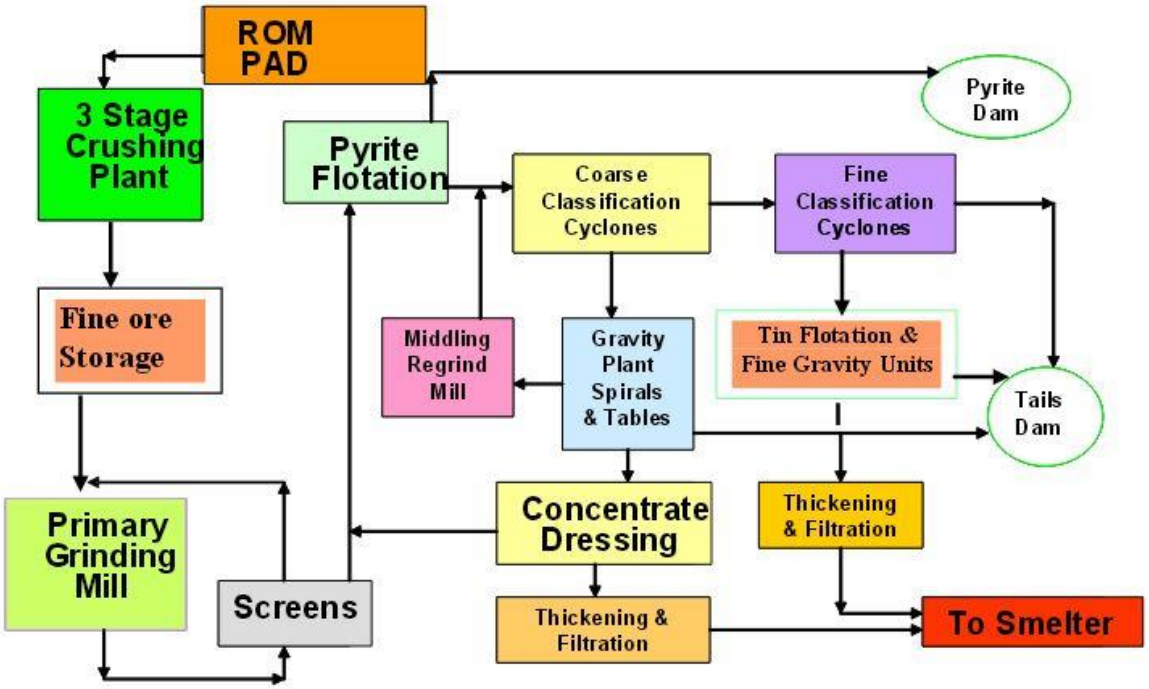

Figure 1.5 Tin processing example; (Hard-rock mining), starting with Run of mine Stockpile (ROM PAD) at the top, to the smelting stage at the bottom. Basically, there is a possible release of tin or related metals at every stage beyond the crushing plant but more so on stages involving waste generation, e.g., conveyance to tails dam. (Source: ITRI, 2012)

1.3.2 Drainage from abandoned tin mines and acid mine drainage

In an ideal complete processing, there would be no useful metals of industrial significance left over after processing. Basic waste products of the process include soil, sand, and small stones that have been rejected during extraction and concentration stages. Normally this constitutes a large amount of the material waste, whose environmental impacts largely depend on the methods of waste disposal employed by a particular mining entity.

However, slag is also produced during smelting and refining stages as a waste product. The slag may have some heavy metal contents and compounds that are potent pollutants to surface water (Kroschwitz and Howe-Grant, 1993).

Acid mine drainage

Acid mine drainage (AMD) is a discharge of commonly acidic, metal-rich water as a result of chemical reactions between rock material, usually containing sulphur-bearing minerals.

While metal-rich acidic drainage may naturally occur in mineralized earth structures that have not been subjected to mining, mining is known to exacerbate disturbances that cause AMD mainly due to rock element exposure to air and water in affected rock structures (Akcil and Koldas, 2006). Some yesteryear mines were engineered in a way that uses gravity drainage of water from mine pits, to avoid pit flooding and to reduce costs associated with mechanical drainage. Consequently, water polluted by metals, acid and other mine-related pollutants can be drained away into streams, rivers and lakes downstream of the mine (Akcil and Koldas, 2006).

AMD can lead to very low water pH, elevated heavy metal concentrations and general pollution and discoloration of freshwater, causing destruction to aquatic life and rendering the water unsuitable for a host of uses. In many countries, including Zimbabwe, there is a big mining-related problem in the form of uncontrolled or poorly managed discharge of contaminated water and decant from some abandoned mines (Banks et al., 1997; Pulles et al., 2005). This is what is usually termed "post operation AMD". It is likely to affect water and environmental quality negatively, depending on the nature of the mineral associated with the mine, as well as the methods of mining previously employed.

Mines that were unexpectedly and indefinitely closed, as was supposedly the case with Kamativi back in 1994 (The Chronicle, 2015) are likely to have undocumented and unmonitored effects of AMD. In most developed countries and many modern mines across the word, mines use predictive geochemical sensitivity analysis tools to determine whether harmful environmental effects may happen after closure of a mine (Castendyk and Webster-Brown, 2007). Modelling software such as PHREEQC, provides useful geochemical calculations that employ monitoring data to project levels of metals that could accumulate at time of closure, their speciation, behaviour when reacting with local conditions, and fate of transportation (Parkhurst and Appelo, 2013).

Since the EMA act of 2002 came into effect more than 10 years after Kamativi operations were indefinitely suspended, there has been neither documentation nor evidence from all enquiries I made that point to any EIA having been carried out on the mine. There is also no EIA recorded for the town or its water and effluent management system. The Zimbabwe government and local mining companies have made efforts to combat potential negative environmental effects of mining activities especially in active mines. However, entities such

as the Kamativi Tin Mine operated and closed before there was a legal requirement to carry out an EIA, as is currently required. This requirement is the equivalent of New Zealand's Assessment of Environmental Effects (AEE) under the Resource Management Act (RMA) (1991).

Mine closure and effects on water management have generally been a source of social and environmental vulnerability especially in developing economies like Zimbabwe's, where the costs associated with reclamation may be prohibitive. Extreme pH values, elevated heavy metal concentrations, foul smelling or dark coloured water, destruction of aquatic habitats, and so on, are some of the common effects of AMD (Akcil and Koldas, 2006).

1.3.3 Tin mining and potential health effects

Tin is a silvery, white metal that is not readily oxidised and is fairly resistant to corrosion due to an oxide layer that covers it (Thomson, 1984). While tin would normally not be broken down by water, it is susceptible to strong pH conditions and will break down in the presence of high alkalinity and strong acids (Howe and Watts, 2005). In this form, it can potentially bind to organic substances forming organic-tin compounds that are highly toxic to humans (Table 1.1). Organic-tin compounds can be taken up mostly by ingestion (Hem, 1992; Kimbrough, 1976; Mweembe & Munkuli, 2005).

Table 1.1 Known Health Effects of Organic-Tin and Related Compounds

Short term effects	**Chronic effects**
Eye and skin irritations	Depressions
Headaches	Liver damage
Stomach-aches	Malfunctioning of immune systems
Sickness and dizziness	Chromosomal damage
Severe sweating	Shortage of red blood cells
Breathlessness	Brain damage (causing anger, sleeping disorders, forgetfulness and headaches)
Urination problems	

Note. Adapted in part from "Analysis of environmental pollution in Sundarbans," by Awal Mohd Abdul, 2014, American Journal of Biomedical and Life Sciences, Vol. 2, pp. 98-107.

Tin in its mineral form (cassiterite) does not pose a danger to living organisms. However, the toxic organic-tin compounds tend to be bio persistent in the environment as most microorganisms struggle or cannot break them down. They tend to accumulate in sediments and soils for several years, causing a gradual rise in organic-tin concentrations which can spread through the water systems when adsorbed on sludge particles. Organic-tin is dangerous to aquatic ecosystems, particularly to fungi, algae and phytoplankton. Death of phytoplankton may reduce oxygen levels in the water. Secondary products may be toxic to fish as well. Their effects include disturbing growth, reproduction, enzymes and feeding patterns. Exposure is usually in the top layer of a water body, where organic-Sn accumulates (Howe and Watts, 2005).

1.4 Kamativi Tin Mine

This research focuses on the quality of water in Kamativi, a mining town whose water supply system, albeit reticulated, has resorted to providing untreated water after suspension of mining operations in 1994 and subsequent economic decline. It had that unenviable transition from being a vibrant mining community with properly monitored and treated water, to a residential area without the economic means to support its vital infrastructure, including the water supply system. Kamativi developed because of the mining of tin and related minerals for about 58 years before 1994, when operations were indefinitely suspended due to low tin prices at the time. As of 2017, the mine is proposed to reopen "soon" (Kazunga, 2017).

1.4.1 Geography of Kamativi

Kamativi lies in north-western Zimbabwe under the Hwange District in the province of Matabeleland North (see Figure 1.6). Locally, the entire town is commonly referred to as "Kamativi Tin Mine".

Figure 1.6 Location of Kamativi in north-western Zimbabwe (Google Maps, 2016).

Figure 1.7 Satellite image of the Kamativi area showing dense bush and waterways (Google maps, 2015).

The greater Kamativi area in which the town and mine are located is characterised by some hilly terrain, approximately 144 km^2 in size, with numerous valleys and some swamps. Several small rivers run through the town and the Gwayi River, which is a major feature in the province, flows past the south of Kamativi, about 14 km away. The area has a very scenic landscape covered in some dense bush over a brief mountainous terrain, which is a stark contrast to the bordering areas of the larger district around it, i.e., Hwange, which tends to be mostly savannah woodland. According to the oral history of the local BaTonga people, the town's name is related to that geographical state. The valleys form pools during the rainy season and one Tonga term for pools is "matibi". They therefore called the area "ka-matibi" meaning a "small place of pools". The number, volume and lifespan of these pools vary widely each year, depending on rains received, but a few are fairly permanent. Of note is the main Kamativi dam (pictured in Figure 1.8) which is the main source of water.

Figure 1.8 A view of Kamativi main dam from the north-eastern end.

1.4.2 Town administration and challenges

The Kamativi area is quite underdeveloped, by Zimbabwean standards. The rural areas surrounding the town depend on it, both as a trading centre and a connection point to the rest of the country. The town hosts the local area's radio, television and mobile phone signal transmitters, a few convenience stores, a hospital, police station, local council offices and three schools. The Hwange District Council currently runs the administration of the town, following temporary relinquishment of responsibilities by the Zimbabwe Mining Development Corporation (ZMDC); this includes the water supply system, which uses surface abstraction from a local dam. The greater Kamativi area is estimated to have a population of just under 7000 people (Zimstats, 2013) with 4000 living in the inner town. Since the mine was the main source of economic income for people, its closure led to deterioration of everything in Kamativi and water problems have dogged the town ever since. There have been several reports about poor water quality and availability. For example, *The Chronicle* has published articles on the looming health problems due to the erratic water supply and residents using raw water to meet domestic needs (Ncube, 2015). While frequent shortages of water in reticulated systems are not unusual in Zimbabwe, the lack of a functional treatment and monitoring system for water in Kamativi makes it particularly vulnerable as an urban community. The storage and treatment facility is old and suffers from lack of maintenance and funding. Dosage of water treatment chemicals may or may not be effective as there is neither sustainable supply nor documented quality control in place to date. The need for water understandably overrides the safety concerns sometimes, and for Kamativi, the actual deviation from potable water standards is relatively unknown or at least not documented.

1.4.3 Mining and its potential environmental effects

The main metal mined at Kamativi was tin. There are other metals that were either produced as by-products from processes similar to those discussed earlier on in this chapter or extracted independently, depending on demand. The chemistry of the rocks in the Kamativi area is used in this research to decide on the likely contaminants that the mining process could have released into the environment and water (Table 1.2).

Table 1.2 Main minerals present in Kamativi (ZMDC, n.d) *(pictures source; mine_data.org)*

Sample picture	Mineral ore
	**Tin (Sn)** Sn minerals, cassiterite (SnO_2), are present as pegmatites within granite intrusions. Also exists as large alluvial deposits especially on the eastern side of Kamativi mine.
	**Tantalum (Ta) and niobium (Nb)** The minerals are present mainly as wodginite ($Mn^{2+}Sn^{4+}Ta_2O_8$) and columbite ($FeNb_2O_6$). Ta and Nb are produced in Kamativi as by-products of the tin processing.
	**Lithium (Li)** The most common minerals are zabuyelite (Li_2CO_3), amblygonite ($LiAl(PO_4)F$) and montebrasite [$LiAl(PO_4)(OH)$]

The mining process in Kamativi used large volumes of water and in addition to the mineral processing, underground mining shafts also accumulated water due to the high water table, and this water needed to be pumped out daily (personal communication, S. Ndlovu, April 21, 2016). Therefore, this is likely to have created a great deal of mixing between surface water and ground water in the water bodies close to the mine. There is also possible contamination as a result of release of toxic metals from the production process. Pulles et al. (2005) alludes to the fact that toxic chemicals are used for leaching purposes in the mining processes, in refinement and found in waste. However, without proper monitoring data, the extent of the problem is hard to estimate. That creates a concern, especially when such a mine is abandoned without any impact assessment and people continue to reside there and consume water from local sources.

From observation, in Kamativi, there are still mine tailings and dumps of pegmatite boulders from tin, tantalite and other minor precious metals. Tantalum oxide is said to be very

insoluble, so that there is almost none to be found in natural waters (Thomson, 1984) but the situation could be different in disused mine excavations, which are now part of the Kamativi waterways. There exist mine shafts in Kamativi near the main dams, as well as disused open cast pits, most of which are now part of the water system as they exchange flow with the natural waterways including the former Kamativi River that flows to the Kamativi main dam. The mine was closed indefinitely (Ncube, 2015) but no known study has been done on the effect of the remaining structure, mine dumps and other mine-related effects on the water and environment.

1.4.4 Economic effects

Mining was the main economic pillar of Kamativi. Historically, the town predominantly housed miners and their families but since its closure, formerly-employed inhabitants include civil servants and those working for NGOs, such as churches. The greater number of residents, over 95%, comprise former miners, new settlers and general people who are either fishermen or subsistence farmers from nearby villages (personal communication, town official, name withheld, February, 02, 2016). Corn (maize) is the main crop that is cultivated despite the region not being a good agricultural area, due to erratic rains.

In light of the above, Kamativi is characterised by poverty. The council that runs the town is on a shoestring budget, as a large number of residents cannot afford to pay their rates on time, if at all.

1.4.5 Kamativi water supply system and its problems

Kamativi uses surface abstraction to pump water from the Kamativi main dam (Figure 1.8) to a storage and treatment facility in the town centre. Several times, reports have been made about the water pump in the town breaking down and residents having to live with no running water for several months. This is a frequent and known problem that some donors have tried to rectify by providing new pumping equipment. During downtimes, people normally source water directly from the dam above or a few boreholes. It is common sight to see women carrying 20-litre containers of water often for long distances to their homes many times a day in the blazing heat. The dam is also a home to crocodiles, fish and other aquatic organisms. Cattle from surrounding villages and other animals are also frequent visitors to the Kamativi dams, especially during the dry season when the rest of the district is significantly dry (Ncube, 2015).

The main problem with Kamativi's water supply is that the lack of economic input due to closure of the mine, and the general economic decay in Zimbabwe has caused, among other things, collapse of water provision infrastructure. This has led to critical steps in the water treatment process being skipped or (indefinitely) suspended, as shown by differences between the processes in Figures 1.9a and 9b.

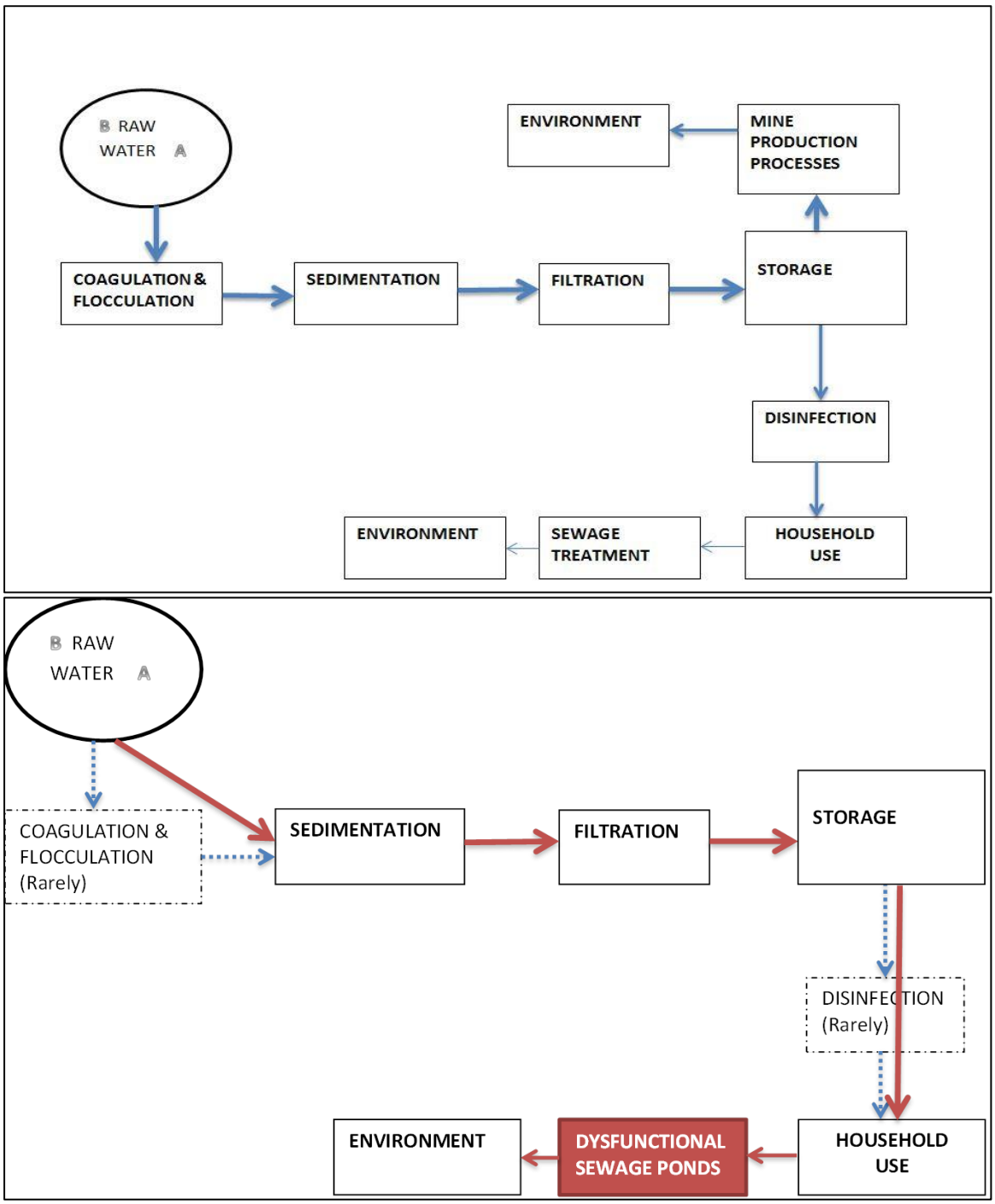

Figure 1.9a (top) and 9b (bottom). Observed interpretation of the Kamativi water supply system basic design (9a) and the current mode of operation (9b).

Figure 9a-b was drawn from my physical observation of the water supply system in Kamativi between April and July 2016 and confirmed by information supplied by members of staff on duty at the water supply stations during the sampling period. The coagulation and flocculation process which is aimed at mainly eliminating solids and turbidity in the raw water was deemed untenable due to lack of money to procure alum (aluminium sulphate), which was the main agent used to flocculate solids during coagulation. The sedimentation and filtration processes look functional on paper, but lack of proper maintenance and replacement of worn-out components mean that those processes are also very inefficient. The pumping capacity of the available pumps is low, and hence there is little turnover time, with very little time allowed for the sediment in the water to settle. Funding issues too mean that there is an inadequate or non-existent supply of chlorine for disinfection. The sewage plant, further discussed below, in also in a dysfunctional state.

While water availability is a conspicuous problem, the water *quality* problems are not, due to lack of monitoring and actual data. Residents in Kamativi may know that the water is not suitable for drinking but there is no readily available information on the actual water quality, which is a critical issue.

1.4.6 Potential environmental effects on water, outside mining

Human and animal waste

The Kamativi main dam is not protected from intrusion, be it from people, or wild and domestic animals. Fishing activities, watering of livestock and sometimes even laundry activities do take place on the shores of the dam. The town's water availability issues mean that water for flush toilets is not always available and open bush defecation is practised in some cases. When some residents frequently resort to using unconventional systems such as relieving themselves in the bush, it is likely to present a contamination risk to surface water, especially during the rainy season when water from surrounding areas is washed into the local reservoirs. There are therefore many reasons to be worried about the microbiological quality of the town's water, considering that there is no consistent disinfection taking place.

Sewage

The town was built equipped with a fairly modern sewage system (at the time) which services the higher density residential areas, while the lower density homes typically have independent septic tanks for each household. While access to the sewage plant is restricted (essentially prohibited) the workers at the town's water department freely say that it is totally dysfunctional (personal communication, identity withheld, 2015). There are not enough funds to run the sewage plant, they say, and waste water is just left there to accumulate as solids are allowed to settle, while the fluid will later seep out of the system, presumably into the environment. The extent of the functionality cannot be ascertained without physically assessing the sewage plant. It is believed to be another potential source of pollution to the water in the area. Both the water supply and the waste water treatment systems are suffering from poor maintenance and reticulated water shortages. There is currently no laboratory or facility capable of testing and monitoring water quality within the town. The possible impact from the town's sewer system on the quality of a nearby dam was included in the research.

I investigated the water problems faced by Kamativi, with a bias towards quality assessment, benchmarking against the Zimbabwean water standards and guidelines which are similar to those provided by WHO.

1.5 Aims and Objectives

The main aim of the research is to determine the status of Kamativi's drinking water quality, comparing it to Zimbabwe's drinking water standards and guidelines, and to identify the source of any noncompliance problems and to propose corrective measures.

In order to achieve this aim, the following objectives were undertaken:

- measurement of physico-chemical and microbiological water quality indicators in key water bodies in the Kamativi area
- identification and quantification of mining-derived trace elements in these water bodies
- comparison of results obtained with Zimbabwean water quality standards and guidelines
- identification and proposal of practical solutions.

Data gathered from this exercise can potentially be used not only to inform on the extent of water quality contamination, but also to demonstrate the need to constantly monitor water quality in Kamativi.

2.0 METHODS

2.1 Field sampling

Sampling of selected water sources at Kamativi was done during part of the wet season (April) and part of the dry season (June–July). Seasonal scheduling was aimed at obtaining a balanced representation on general water quality which may be affected by prevailing weather conditions. Two separate trips from New Zealand to the research location in Zimbabwe were made, one in April and another in July as shown in Table 2.1.

Table 2.1 Sampling and data collection timeline

Schedule	April				May				June				July				August			
	Week				Week				Week				Week				Week			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1st TRAVEL TO RESEARCH LOCATION																				
Locating sites, acquiring local authority permissions & logistics																				
Sample collection & in-situ testing																				
1st RETURN TO NEW ZEALAND																				
Laboratory tests and analysis on Imported Samples																				
2ND TRAVEL TO RESEARCH LOCATION																				
Sample collection & in-situ testing																				
Lab Tests and Analysis																				
2nd RETURN TO NEW ZEALAND																				

Due to the remoteness of Kamativi and the need for lengthy air travel, field visits were limited to two, i.e., once in April for the wet season and once in the period June–July for the dry season. The duration of stay was limited to 28 days in April and 54 days in the dry season (4 June–28 July 2016) in order to keep within the limits of the New Zealand Development Scholarship conditions.

2.1.1 Site selection and sampling programme

Eight sampling sites, comprising all major surface water sources in Kamativi and two controls, were identified with the help of various local residents and Council staff (see Figure 2.1). The two control sites are located upstream of the former mining area of the town. The sampling points are shown in Table 2.2.

Table 2.2 Sampling sites in Kamativi and its periphery

Site	Local Name	Site Descriptor
A	Kamativi main dam –eastern	Main water reservoir.
B	Kamativi main dam-western	Linked to A by a channel through a built up border ridge.
C	Quarry	Disused opencast quarry pool on the eastern side of the mining area.
D	Syabunyangu Stream	Part of the old Kamativi River. It runs past mining grounds to Kamativi dam.
E	Number 4 Dam	No current prescribed use but was a backup supply for the mine.
F	Household tap	Water drawn from a random domestic tap from the main residential area.
G	Kamabimba River	Upstream, 5–7km south-east of Kamativi.
H	Ward 20 Dam	Control site on the eastern side of Kamativi. Used by some residents during water cuts.

Sampling was successfully done at all eight sampling sites, with four x 50mL water samples per site collected, on the first trip. During the second sampling visit, the sites were cut down to five, after two rivers (sampling points D and G) dried out, and coincidentally there was no tap water availability (sample point F) during the second trip's sampling time.

At each site, field measurements were taken for temperature, pH, conductivity, dissolved oxygen, nitrate-nitrogen and phosphate. Fresh samples were collected for *E. coli* and coliform bacteria, and four x 50 mL samples were collected and stored below 4^{o}C prior to being transported back to New Zealand for chemical analysis.

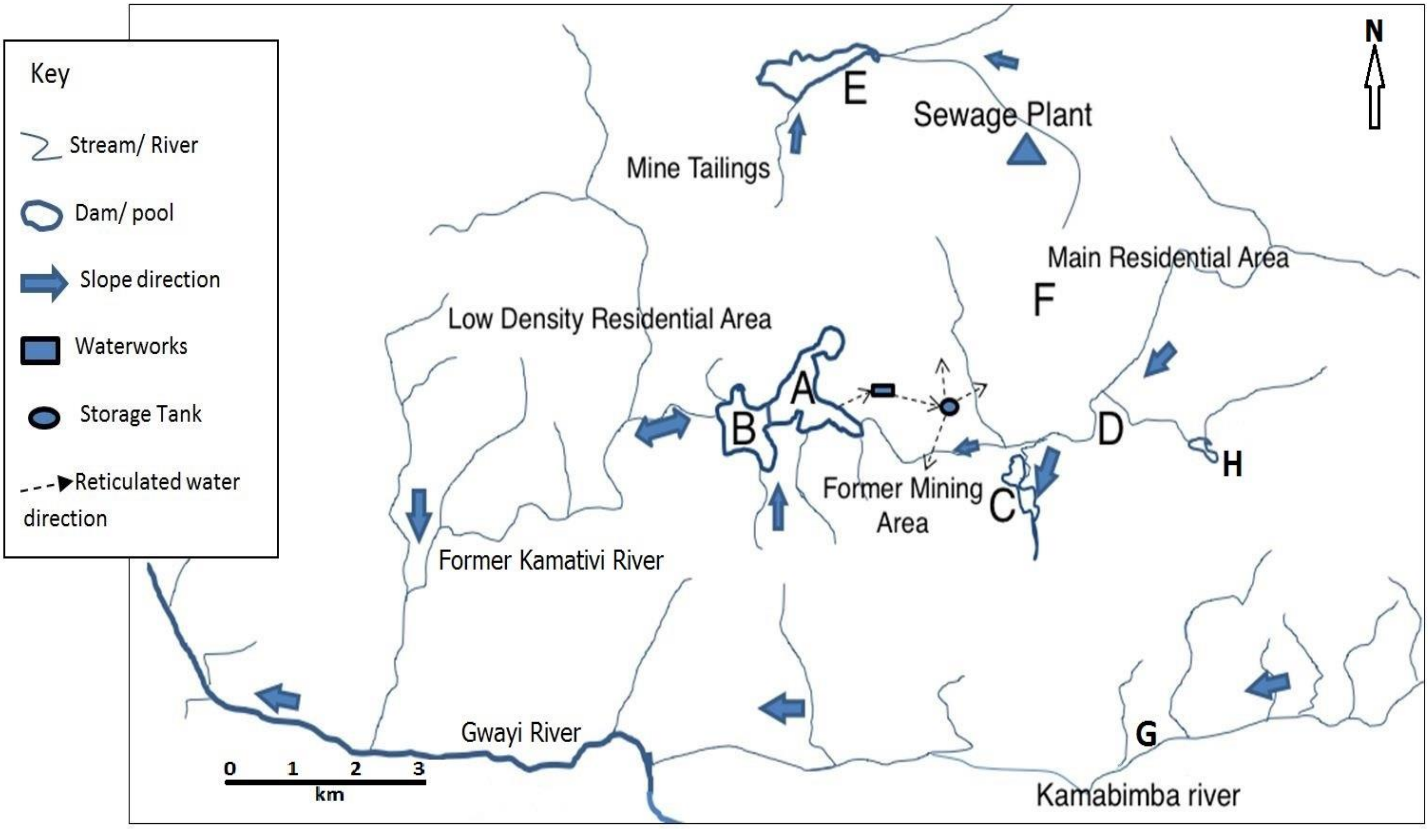

Figure 2.1: Location of sampling sites A–H in Kamativi. Sites A–F are the most accessible surface water sources.

Site Descriptions

Site A

Figure 2.2 Site A: Eastern wing of the Kamativi main dam as seen from the north-eastern end, facing south east.

Site A is the current main water reservoir for Kamativi. The dam is approximately 2.5 km from the tin-mining area, for which it was a strategic source of water for the production process of the mine. According to Phiri S. (personal communication, April 21, 2016, Kamativi waterworks), the dam was formed by blocking off Kamativi River at the inception of the mine, to form a reservoir to supply the mine with process water for its operations. It is 874 m above sea level and can hold up to 490 megalitres of water. Water is abstracted using electric powered pumps through piping of about 250 mm diameter and brought up the hilly terrain to a water treatment plant where it is subjected to filtration, coagulation and flocculation before being relayed onto a giant reservoir tank whose exact volume could not be ascertained at the time of sampling. From here the water enters the distribution network of smaller pipes to the various mine stations and domestic establishments as per demand.

The area around the Eastern dam is covered in evergreen grass and the shores are fairly free from tall vegetation. The dam is separated from an adjacent dam downstream by a wall and flood gates built to control the water level in case of heavy rains or similar phenomena (Personal Communication. Phiri. R., April, 21, 2016, Kamativi water works). Different types of fish species, crocodiles and a limited number of hippopotami inhabit this dam.

Site B

Figure 2.3: The western wing of Kamativi main dam as seen from an elevated point on the north-west, facing south east

.

This dam forms the downstream part of the blocked and widened section of the former Kamativi River. It has a greater abundance of wild life including fish, crocodiles and birds, due to it having relatively less human presence in comparison to the eastern wing of the dam. There is dense vegetation all around the shores of the dam, including bushes and trees. The shores are also steeper, with bushes as compared to the flat grassland of the eastern wing. The water looks darker from both satellite imagery and eye observation and is said to be deeper by local fishermen. This dam is only used as a water source by people residing on the western part of Kamativi dam when their taps run dry, which is common due to frequent breakdown of the aging equipment (Ncube, 2015).

Site C

Figure 2.4: Part of the Quarry site dam in Kamativi as seen from the east facing west
*Note. Image by W. Hampel, 2015 (*http://www.mindat.org/loc-31358.html*) Copyright 2015 by the Photographer, Used with permission.*

This is a large pool of water in a former opencast quarry. Water flows into this quarry from various points but there is no outlet coming from here. There is no prescribed use for this water body, but like all others, it is used by nearby residents when tap water is absent, e.g., during water cuts or the frequent equipment breakdowns.

Site D

This is a seasonal waterway, locally known as Syabunyangu Stream, a remnant of the former Kamativi River, which has since been renamed by locals. It runs down nearby hills aggregating into a bigger river as it goes through part of the residential area, past mining grounds, and finally empties into the eastern wing of the Kamativi dam.

Site E - Number 4 Dam

Figure 2.5: "Number 4" Dam which was sampled as Site E. The picture was taken from the western end of the dam, facing east.

This is located to the North of Kamativi in close proximity to the mine tailings. It is a major source of water for livestock coming from the nearby villages. The dam is also used by locals for irrigation and fishing. It is perceived as being less risky for fishermen due to the low population of crocodiles despite the fish availability being low as well, hence making it less profitable than sites A and B.

Site F - A household tap

Kamativi's main residential units fall on the north-eastern side of the town. Tap water is currently rationed and supplied to the almost 3000 units twice a day for a period of about 1–2

hours in the morning and late afternoon. The reticulation system is old, and problems ranging from faulty equipment to power failure are common occurrences. A household tap from Unit Number A7 was selected for sampling.

Site G - Kamabimba River

Figure 2.6. A part of Kamabimba River as seen from the western side, facing east

This river flows from the south-east to the south-west of the town where it eventually integrates into the much bigger Gwayi River. The upstream point G shown on the map was selected as a control as it is far from any influence from Kamativi town, approximately 9 km to the south-east. It is located in a wild valley setting with no nearby human settlements. Due to the El Nino-induced drought of the 2015–2016 rainy season in Southern Africa, Kamativi recorded very low rainfall in the rainy season, including April 2016 (UNICEF, 2015). Kamabimba River had no flow during the winter (dry) period in June–July hence sampling was only done for the wet season in April.

Site H - Ward 20 Dam

This dam is relatively small compared to others mentioned above and is located to the east of the town. It receives water from many small streams coming from the countryside areas lying to the east of Kamativi. Flow pattern and geographic location suggests that the dam is unlikely to have any influence from the mining area, hence its selection as a control site.

Livestock from some rural areas do, however, frequent this place for drinking. About one hundred rural homesteads on the eastern periphery of Kamativi also draw water from here for domestic use. This was established from personal communication with several villagers seen drawing water from the dam on four occasions during sampling.

2.2 Sampling methodology

For all sites, a relatively similar sampling method was employed. As these sites are used as water sources at one point or another, with the exception of Syabunyangu stream (D) and Kamabimba River (G), existing abstraction points were used. This was also done to avoid a potential of conflict with wildlife by venturing further into the water body without adequate protection. At sites D and G, random points were chosen, along the river or stream flow for sampling. Samples were collected with the assistance of water reticulation staff from the Hwange Rural District Council. Fresh 50 mL samples were collected from each site for *E. coli* and coliform analysis at a laboratory in Bulawayo, Zimbabwe, approximately 300 km away from Kamativi. Four x 50 mL of water per site were collected and stored below 4^{o}C prior to being transported back to New Zealand for further chemical analysis.

A sampler was used, comprising a polypropylene container with a handle of the same material fixed to it, and grab samples were collected by scooping water off the surface and filling up a 50 mL centrifuge tube. The first scoop was used to rinse the sampler and centrifuge tube twice before the collection of the actual sample, as recommended by Gardner (1986).

For each site, four x 50 mL tubes of water were collected.

1 x unfiltered water for analysis of major anions
1 x unfiltered water for major cations and total acid soluble trace metal concentrations,
2 x filtered (through 0.45 µm Millipore membranes) water for dissolved trace metals.

Each sample was labelled with the following upon collection:
A site code (i.e. A-H), date, what it was for and whether it had been filtered or not, e.g., MI (major ions), TMUF (trace metals unfiltered) and TMF (trace metals filtered).

Samples were put into two clean separate bags according to intended use, and then both put into a single bag that was later placed in a hard-plastic container filled with a hydrous phyllosilicate mineral (vermiculite) to guard against spills, as per IATA guidelines for hazardous items packing. The container was sealed using packing tape and samples imported back to New Zealand under a Ministry of Primary Industries (MPI) permit number 2016059753 for importing laboratory specimens. The samples were stored in the PC1 Waterways Centre laboratory at Lincoln University.

2.3 In situ measurements

On site measurements were taken for temperature, pH, conductivity and dissolved oxygen using a HACH HQ40D multimeter (probe meter). The probe was dipped directly into the water body and readings for each parameter recorded after the measurement had been taken.

Phosphate and nitrate concentrations were measured using a HACH DR890 colorimeter from fresh samples at the end of the sampling day during the June–July visit, but this was not possible on the first trip due to the colorimeter being held up by customs and border officials at the airport. Nutrients were instead analysed using the same technique, on four-week-old samples, later, back in New Zealand.

2.3.1 Nutrients

Nitrate concentrations were analysed using the cadmium reduction method (using powder pillows) on a HACH DR890 colorimeter (APHA, 1995). All samples for nutrient analysis were initially filtered through 0.45 µm Millipore membrane upon collection. An outline of the procedure carried out is given below:

- Two sample cells were each filled with 10mL of the sample, filtered through a 0.22 µm Millipore membrane. One sample served as the prepared sample, while the other was used as the blank.
- A nitrate reagent sachet (powder pillow) was then added to the prepared 10 mL sample and shaken vigorously for 1 minute followed by an allowance of 5 minutes' reaction time. Tissue paper was used to gently wipe clean the surface of the sample cell to ensure that the surface was free of any liquid or dirt.

- The blank was placed into the cell holder on the colorimeter and the instrument was zeroed. The prepared sample was then put in and a reading of NO_3-N in mg/L was taken.

Phosphate concentrations were analysed using the same instrument as for nitrates by the ascorbic acid method (APHA, 1995) and the steps done are as follows:

- Two sample cells were filled with 10mL of a sample that was filtered through a 0.22 µm Millipore membrane.
- A phosphate powder pillow was added to one sample before shaking for 15 seconds then allowed to settle within a 2 minute reaction period.
- The second sample cell served as the blank and was used to zero the colorimeter, as done with nitrate above.
- After 2 minutes had elapsed, the first sample was placed into the cell holder and a reading taken for phosphate (PO_4^{3-}) in mg/L.

2.3.2 Turbidity

Turbidity was also analysed using the HACH DR890 calorimeter by selecting program 95 on the instrument mode.

- Samples for turbidity were not filtered upon collection. The sample cell to be read was filled with 10mL of the unfiltered sample. A second cell was filled with a sample filtered through a 0.22 µm Millipore membrane. This was used as the blank to zero the instrument.
- Tissue paper was used to gently wipe clean the surface of the sample cells to ensure that the surface was free of any liquid or dirt. Then the blank was placed into the cell holder on the colorimeter and the instrument was zeroed.
- The unfiltered sample cell was then put in, and a reading in Formazin Attenuation Units (FAU) was recorded.

The detection ranges for the methods used are given in Table 2.3.

The HACH DR890 colorimeter is factory programmed for analysis of various parameters including nitrate, phosphate and turbidity. Each parameter has a programme number that is selected from the menu prior to testing for it, as shown in Table 2.3.

Table 2.3: Detection range for nutrients and turbidity

Parameter	Mode number	Range/ limit	Method
Nitrate	54	0.4 to 30.0 mg/L NO_3N	Cadmium reduction
Phosphate	79	0.02 to 3.00 mg/L PO_4	PhosVer®3 (ascorbic acid method)
Turbidity	95	0 to 1000 FAU (limit of 21 FAU)	Absorptometric method

2.3.3 Faecal bacteria

An *E. coli* and faecal coliform count was done within 24 hours of sampling at an ecotoxicology lab of NUST University, 300 km away from the sampling site.

Commercially prepared *E. coli*/ coliform 3M petrifilm plates were used, one per sampling point. Each one of them was inoculated with 1 mL of the respective sample using a sterile glass pipette tip. This was followed by an incubation period of 24 hours at 37.4^{o}C.

An indicator dye in the plate coloured *E. coli* colonies blue, and faecal coliform colonies were red. A colony count of each, in colony forming units/mL (CFU/ml), was then recorded.

2.4 Laboratory analysis

Trace elements (Sn, Li, Ta, Nb, Pb, W, As, Al, Fe, Cu, Zn and Mn) and some major water ions (stated in section 2.4.1) were analysed on imported samples using methods that included inductively coupled mass spectrometry (ICP-MS), infrared gas analysis (IRGA) and high pressure ion chromatography (HPIC), as outlined in the following sections.

2.4.1 Major ions

Bicarbonate ion (HCO_3) also known as hydrogen carbonate was analysed in the form of dissolved inorganic carbon (DIC) during the first week after arrival back in NZ, at the

Waterways Centre Laboratory at Lincoln University using IRGA. Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} were analysed using ICP-MS together with trace elements (see section 2.4.2) at the University of Canterbury's Chemistry Department. The anions Cl^{-} and SO_4^{2-} were measured using HPIC at Lincoln University's Chemistry Department.

Dissolved Inorganic Carbon (DIC)

DIC is a sum of inorganic carbon variants in a solution. These include carbon dioxide, carbonic acid, bicarbonate anion, and carbonate. Thus:

$$DIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \text{ where } [CO_2^*] = [CO_2] + [H_2CO_3] \quad \text{(eqn 2)}$$

This is, in fact, part of the pH-driven chemical equilibria:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad \text{(eqn 3)} \quad \text{(APHA, 1995)}$$

The concentrations of the different constituents of DIC depend on the pH, hence when measuring DIC, the sample is acidified (thereby increasing $[H^+]$) to drive the equilibria towards CO_2, which was in turn measured, in this case by an Infrared Gas Analyser (IRGA) (APHA, 1995). Prior to analysis, each water sample was acidified with phosphoric acid, under a nitrogen headspace. This acidification converted DIC in the sample to CO_2, which equilibrates with the nitrogen headspace.

The procedure for each sample was carried out as follows:

- A 50 mL syringe was weighed and its weight recorded. Five mL of sample was drawn into the syringe, followed by 50 mL of nitrogen gas. The syringe was weighed again (to get the exact volumetric mass of the contents by subtracting the empty weight later).
- A 1 mL syringe was filled with 0.2 mL concentrated phosphoric acid (85%) and then connected to the 50 mL sample syringe using a short connector tube of about 25 mm. The exterior was rinsed with deionized water. The 50 mL syringe was held uppermost then the acid in the 1mL syringe was injected into the larger syringe. Mixing was done by pumping the 1 mL plunger. Both syringes were left connected and placed on the mixing wheel for 1 hour.
- After mixing, the 1 mL syringe was removed and a 5 mL syringe that had been flushed with nitrogen was connected to the 50 mL syringe. Five mL of gas was pushed from the 50 mL syringe into the 5 mL syringe. The sample from the 5 mL syringe was then

injected rapidly into the gas stream of the IRGA and the peak height shown on the chart recorder was entered onto a spreadsheet to calculate the adjustment factors by volume (Table 2.4) and weight needed to calculate concentrations of DIC. The procedure followed was obtained from the Lincoln University Lab Standards Operations manual.

The detection range was 0 to 10mmol/L. Adjustment factors are shown in Table 2.4.

Table 2.4 Adjustment factors

Standard	Empty weight (g)	Full weight (g)	Actual weight (g)	Adjustment factor (5/wgt)	Adjusted concentration
1 mmol/L	26.32	31.34	5.02	1.00	1.00
2 mmol/L	26.30	31.37	5.07	0.99	1.97
5 mmol/L	26.31	31.42	5.11	0.98	4.89
10 mmol/L	26.23	31.32	5.09	0.98	9.82

Chloride (Cl^-) and sulphate (SO_4^{2-})

For Cl^- and SO_4^{2-} analysis, 5 mL sample per sampling site were submitted to the Soil Chemistry laboratory at Lincoln University for high pressure ion chromatography (HPIC) analysis using a Dionex AS-AP autosampler with Dionex ICS2100 and AERS 500 4mm columns.

HPIC is a technique that separates ions or charged molecules in solution according to their ionic charge strength. Charged analytes interact with opposite charges on a stationary phase matrix. This matrix contains charged ionisable functional groups. HPIC can be cationic exchange and/or anionic exchange, where positively charged ions bind to negatively charged exchange resins, while those with negative charge are attracted to the positively charged exchange resins. The ions are either retained or washed off depending on the strength of their charge. Initially, those with weaker charges and therefore binding weakly to the matrix, are the first to wash away. Conditions can be altered as needed to enable washing off of the different strengths of charged ions that bind to the matrix. Altering conditions can be achieved by increasing or decreasing the concentration of exchangeable counter ions, which compete with the charged ions for binding to the resin, or by changing the pH (Jungbauer & Rainer, 2009)

The preparation procedure for each sample was carried out in the following manner.

Unfiltered samples, one from each sampling site, were filtered through 0.22 µm Millipore membrane filters. Clean vials of 5 mL volume were labelled in the order of sampling sites and sampling session from which the samples were taken, e.g., PM1 was the sample from Site A taken during the first sampling visit in April, PM9 was the sample from site A imported from the second sampling trip in June–July, etc. Each vial was filled with 5 mL of the filtered water and the vials were put in a rack then submitted for analysis. Vials had been cleaned by rinsing twice with ethanol then three times with deionised water before being put away the day before use. Labelling code and order was recorded in the lab book as soon as it was completed, to provide a fool proof reference for comparison when results from the lab were received.

Table 2.5 Anion detection limits from High Pressure Ion Chromatography (HPIC) analysis

Cl^-	0.005ppm
SO_4^{2-}	0.05ppm
Br^-	0.02ppm

2.4.2 Trace Elements

Two 10 mL samples for each sampling site A–H were submitted to the Chemistry Department at the University of Canterbury for analysis of trace elements and some cations in the water using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

ICP-MS

ICP-MS is an analytical determination technique for elements. The instrument has a high-temperature ICP (Inductively Coupled Plasma) source and a mass spectrometer. The principle of operation is such that the ICP source converts atoms of the elements in a sample to ions. The resultant ions are then separated and detected by the mass spectrometer.

Sample Preparation

Of the two 10 mL samples submitted from each sampling site, one unfiltered was for analysis of total trace elements in the water, while the other (filtered) targeted only dissolved elements. In the first submission for Wet Season sampling, a request was made for both a quantitative and semiquantitative scan.

The quantitative scan was requested for the trace elements Sn, Mn, Fe, Cu, Pb, Zn, Nb, Li, Ta, W and Pb (sumd 206Pb, 207Pb and 208Pb), while the semiquantitative scan was for every analysable trace element. After the semiquantitative scan from first set of results gave indicative significance of some elements, the requested list was revised to include As and Al in the quantitative scan for the second submission.

Major ions analysed by ICPMS included Na, K, Mg and Ca.

The samples were prepared as follows:

- The first set of unfiltered water was acidified by adding 0.1mL (100µL) of Ultra-Pure (70%) HNO_3 to 50 mL of sample to attain a pH of 1.5
- The acidified water was given a reaction time of 24 hours. After 24 hours, the water was filtered through 0.22 µm Millipore filters and 10 mL of each sample was put into labelled centrifuges of 15mL capacity.
- The second set of samples, for dissolved elements, were filtered at 0.22 µm before being acidified to pH 1.5 by adding 0.02 mL HNO_3 (70%) to 10mL of sample. They were also labelled and put onto a rack for submission.

Table 2.6 Detection limits of major ions and trace elements as derived from ICPMS standard solutions that were run for quality control purposes. The items are listed in alphabetical order.

Al	1 µg/L		Na	1. µg/L
As	0.1 µg/L		Pb	0.1 µg/L
Ca	10 µg/L		Sn	0.1 µg/L
Cu	0.1 µg/L		Ta	0.1 µg/L
Fe	1.00 µg/L		W	0.1 µg/L
K	0.1 µg/L		Zn	1 µg/L
Li	0.1 µg/L			
Mg	1 µg/L			
Mn	0.1 µg/L			

2.5 Quality control

2.5.1 Onsite measurements

Calibration of the HACH HQ40D multimeter probe was done prior to departure to the research site for onsite measurements. Each of the three probes (pH, conductivity and DO) has its own calibration mode which was selected prior to running a "Check standards" verification test for accuracy.

The calibration for pH was done using three commercial standard solutions of pH 4, pH7 and pH10 respectively. A saturated oxygen solution was used to calibrate for DO. It was prepared by filling a 50-mL centrifuge tube with distilled water, followed by shaking it whilst open for 5 minutes. A standard solution of 100 microsiemen/cm (µS/cm) was used for conductivity.

The calibration mode for a parameter was selected as well as the corresponding known values given above, the probe was put into the standard solution, and the instrument ran the "Check Standards" test. This verified the equipment accuracy by measuring a solution of a known value (APHA, 1995). The meter then indicated on the LCD screen that the "Check Standard" had passed.

Had the Check Standard failed, the calibration icon would have appeared on the LCD then recalibration would have been done by keying in the corresponding values to the standard solutions used and saving them to the instrument memory. Prepared standard solutions were taken along during the sampling trip and the above tests were also done in Zimbabwe. The pH probe was kept within a pH 4 solution as recommended by the instrument manual and APHA (1995) to preserve its integrity.

Probes were rinsed briefly prior to sampling using the water to be measured. After taking each reading, the probes were rinsed using distilled water prior to storage and moving on to the next sampling site.

2.5.2 Nutrients and Turbidity

Samples were collected in clean plastic centrifuge tubes, and during analysis clean glass cells were used. Analysis was done in situ during the second trip (June–July). For the April trip, samples were stored in a refrigerator (below 4°C) except during the long flight from Zimbabwe to NZ where storage conditions were uncontrolled.

Accuracy testing was done prior to taking the colorimeter away from the Waterways Centre laboratory to Kamativi. A cell filled with distilled water was used as a blank to zero the instrument and a stock standard solution of known concentration was measured (0.5 mg/L for NO_3-N and 0.05 mg/L for PO_4). Readings obtained were within ± 0.1 of the standard for NO_3-N and ± 0.01mg/L of the value for PO_4. A formazin stock solution of 200 FAU was used to check for accuracy of turbidity measurement – it passed the test. During zeroing and reading taking, the sample cells were tightly covered by the instrument cap

During in situ measurements, a filtered sample without addition of the reagent was used as a blank to ensure that the zeroing captured the characteristic sample being dealt with each time.

Due to Kamativi water being highly coloured, filtered portions of samples were used in place of deionized water to zero the colorimeter during turbidity measurement (APHA, 1995).To enhance reliability of recorded readings, care was taken in verifying data with that on the colorimeter's log system before transferring readings recorded in the lab book to the results spreadsheet on the computer.

2.5.3 Faecal bacteria

The following sterile techniques were followed to avoid contamination and improve accuracy of the test.

Hands were washed thoroughly before and after each sample's procedure. The work surface was swabbed with 70% ethanol before carrying out the inoculation process, left wet and allowed to evaporate dry. Glass pipette tips that had been subjected to autoclaving were used for the inoculation, one for each sample. A control petrifilm was inoculated with sterilized water, previously boiled and cooled. This returned zero count in all cases.

2.5.4 DIC

At the beginning of the DIC analysis procedure, the IRGA was warmed up with a flow of 300 mL/min, for 1 hour, in differential mode. During this stage, the plumbing was arranged so that the nitrogen flow went through all of the reference and sample cells. Flow rate is important and needed to be kept constant during the run and calibration procedures. The pressure on the IRGA was kept ≥ 1 atm by adjusting the flow from the gas cylinder and keeping a 1mL syringe connected to the gas stream outlet of the instrument to prevent

pressure loss. Calibration was done with 1mmol/L, 2mmol/L and 5 mmol/L standard solutions of bicarbonate, see Figure 2.7, and the blanks used were fresh deionized water.

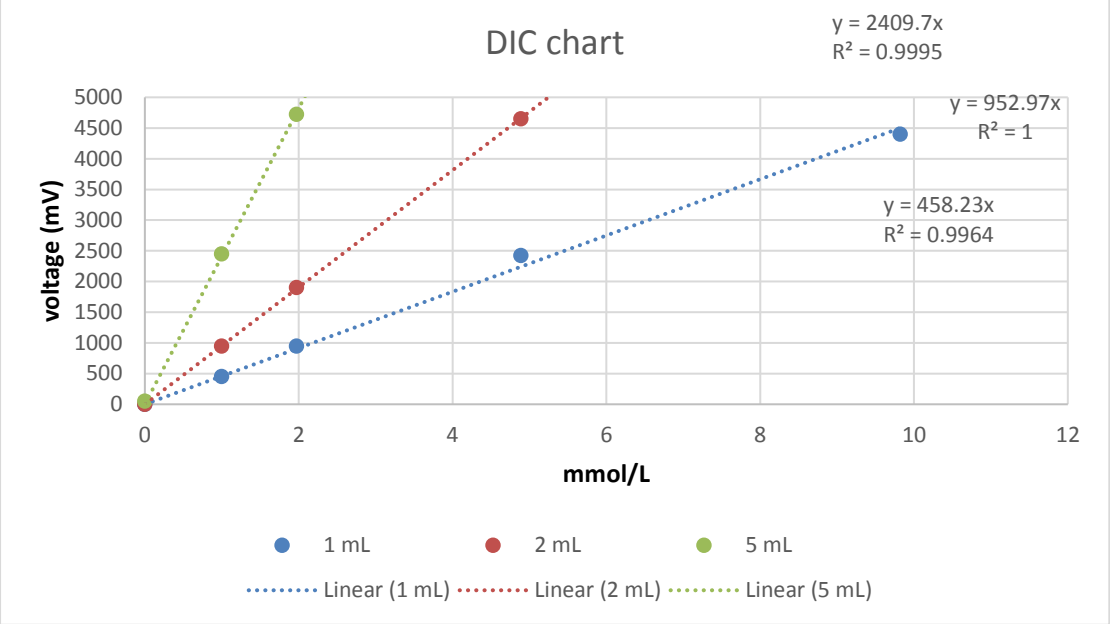

Figure 2.7 DIC calibration chart verifying consistency of peaks recorded against corresponding concentrations of known DIC standards

Since multiple (8) samples were being analysed in one session soon after injection and recording the peak, the 5 mL syringe was removed and replaced with the 1 mL syringe that was kept there until the next (re)injection. Due care was taken to ensure that samples were not contaminated during sampling, transportation, preparation and analysis. As mentioned in Section 2.2, the choice of sampling material was also informed by reliability in avoiding contamination from the environment as well as leakage between samples.

Sample tubes were labelled concisely as indicated in Section 2.2 and submitted along with a form that includes details of the labelling to prevent mix-up errors. Work bench tops in the PC1 laboratory at the Waterways Laboratory have metal surfaces, so plastic trays were used to temporarily place sample racks during preparation as a failsafe measure. The samples were filtered to remove particulates prior to submission. The acid strength was teste during and after preparation to ensure that it met requirements stated in the submission form for ICP-MS. Samples also included a deionised water blank which was used as part of quality control after

the analysis. Results of the blank in both submissions were comparable to those of standards used for testing (see Appendices).

2.6 Water quality standards and guidelines

Zimbabwean water quality standards and guidelines were compared with results obtained from the study for compliance of the tested water. These standards and guidelines are mostly adopted from the WHO health-based guidelines for drinking water (Table 2.7)

Table 2.7 ZW standards and WHO guidelines used in comparison with results from Kamativi (WHO, 2011; ZMDC, n.d; Standards Association of Zimbabwe, 2015)

Element/ substance	Symbol/ formula	Normally found in fresh water/surface water	Limit
Aluminium	Al		0.2 mg/L
Antimony	Sb	< 4 µg/L	0.005 mg/L
Arsenic	As		0.01 mg/L
Barium	Ba		0.3 mg/L
Beryllium	Be	< 1 µg/L	No guideline
Boron	B	< 1 mg/L	0.3 mg/L
Cadmium	Cd	< 1 µg/L	0.003 mg/L
Chloride	Cl		250 mg/L
Chromium	Cr^{+3}, Cr^{+6}	< 2 µg/L	0.05 mg/L
Copper	Cu		2 mg/L
Cyanide	CN^-		0.07 mg/l
Fluoride	F	< 1.5 mg/L	1.5 mg/L
Hardness	mg/L $CaCO_3$		No guideline
Iron	Fe	0.5 - 50 mg/L	No guideline
Lead	Pb		0.01 mg/L
Manganese	Mn		0.5 mg/L
Mercury	Hg	< 0.5 µg/L	0.001 mg/L
Molybdenum	Mb	< 0.01 mg/L	0.07 mg/L
Nickel	Ni	< 0.02 mg/L	0.02 mg/L
Nitrate	NO_3		50 mg/L total NO_3, 10mg/L
Turbidity			5 FAU for treated tap water
pH			6.5 – 8.5
Selenium	Se	< 0,01 mg/L	0.01 mg/L
Silver	Ag	5 – 50 µg/L	No guideline
Sodium	Na	< 20 mg/L	200 mg/L
Sulphate	SO_4		500 mg/L
Inorganic tin	Sn		No guideline
Uranium	U		1.4 mg/L
Zinc	Zn		3 mg/L

2.7 Statistical comparisons

2.7.1 Bar graphs

Bar graphs were plotted to compare calculated means (medians for pH) with each other and with the stipulated guidelines or standards where applicable.

2.7.2 The Wilcoxon–Mann–Whitney test

The nonparametric Wilcoxon–Mann–Whitney test was used for assessing for any significant differences between the results obtained during the wet and dry seasons. It was chosen due to the inability to assume normality on the data obtained. Comparison was between the five sites available for both the wet and dry seasons, i.e., Sites A, B, C, E, and H. This was done with the statistical software 'R'. Testing was done at 95% confidence level, i.e., $\alpha = 0.05$. The null hypothesis is that the parameters are the same during the wet and dry seasons, i.e., there is no significant difference.

The computed p-value (p) of our statistic was used to determine rejection or acceptance, whereby if p computed is less than 0.05, the null hypothesis (H_0), that there is no significant difference between the results of the parameters in the two seasons, is rejected and a conclusion made that a significant difference exists. If p is larger than 0.05, we fail to reject H_0 and conclude that no significant difference exists between the results of the wet and dry seasons.

2.7.3 Pearson correlation coefficients

The Pearson correlation coefficient (PCC) measures the strength of linear associations between two variables. PCC draws a line of best fit scenario through existing data points for any two variables, and then computes a coefficient (r) that indicates how far off these data points are from the ideal best-fit scenario line. The coefficient- r values range from -1 to +1. When r = 1 or -1, all data points lie along the line of the best fit scenario, i.e., there is total positive or negative linear correlation. A positive correlation means one variable increases with a corresponding increase in the other, while a negative correlation value means one variable decreases as the other increase, i.e., they are inversely proportional. Strong linear dependences are those close to 1 and in this research, it was predetermined that strong correlations will be at least r = ± 0.8. "Not a number", NaN represents 0 linear correlations, as computed in the statistical package R.

3.0 RESULTS

3.1 Field conditions during sampling

3.2.2 Wet season

The wet season sampling was undertaken in April. Sites A, B, C and E, which host lentic ecosystems, were surrounded by lush green vegetation and were also receiving inflows from their feeder streams and rivers. It had rained in the previous weeks and there was some flow in the Syabunyangu stream (D) as well as Kamabimba River (G). Temperatures were higher during wet season sampling (22–32°C) sampling than in the dry season (9.5–27.3°C)

The surface of Site C was murky during the rainy season and the dam had higher water levels than seen in the second sampling session. Minor patches of aquatic plants were noticeable on the surface of Site C. There was dense indigenous riparian vegetation along Kamabimba, which makes walking near the banks difficult. No equipment to measure flow was carried and, partially due to the hazard of crocodiles, no flow rate data was taken. The water at sampling point H, which is upstream of the Kamativi River (control), was grey with suspended particles. There was no notable presence of algae observed in the sites visited. The general sampling schedule for the wet season is presented in Table 3.1.

Table 3.1 Wet season sampling schedule

Site	Details
All sites (A-H)	Sampling done 3 times i.e. 5 days apart from the beginning of April 2016. In situ measurements also done 3 times.

3.1.2 Dry season

The dry season sampling occurred during the months of June and July, which corresponds to winter in Zimbabwe. Due to the prevailing El Nino-induced drought at the time (UNICEF & WFP, 2016), the dry season started earlier than normal in 2016 (late April–early May). The water was generally calm at all sites sampled. By the month of June, when sampling commenced, there was no flow in the rivers, i.e., sites D and G (one of the two control sites). Site C had lower water levels compared to the wet season and had a subtle but noticeable outgrowth of water weeds on the surface, not previously observed.

Ambient air and water temperatures were lower in the dry season than in the first visit (Figure 3.3). At Site H, a lot of animal activity was observed, particularly mammals, including domestic cattle, goats, and sheep. The sampling schedule during the dry season is presented in Table 3.2.

Table 3.2 Dry season sampling schedule

Site	**Details**
A, B, C, E and H	4 x in June 4 x in July In situ measurements done 1 x per week for all parameters except *E. coli* and coliforms which were done only twice i.e. once per month
D and G	0 (No flow in the rivers)
F	0 (tap water was unavailable during scheduled sampling days/ times)

3.2 Seasonal water quality

The water quality summary results are presented in Tables 3.3 and 3.4. The sites are presented in the order of relative distance from the mine, with the two controls shown last.

The data presented are means (pH shown as medians) across the sampling periods for the wet and dry season respectively. Full raw data from each sampling day are shown in Appendices 1 and 2. The last two sites (G and H) are controls. Water quality results were compared with the Zimbabwean standards and guidelines (ZW), and the World Health Organisation (WHO) health-based guidelines for drinking water, where ZW standards and guidelines were not available.

Table 3.3 Wet season water quality summary (n=3). Controls are shaded in light green encircled with blue dotted lines.

		Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H
pH		8.46	7.68	7.04	8.28	7.58	7.63	7.18	6.59
DO	**(mg/L)**	11.81	7.63	6.76	11.79	8.42	9.49	11.76	6.51
Temperature	**(ºC)**	26.1	26.0	26.3	26.1	26.6	20.7	26.2	26.4
Conductivity	**(µS/cm)**	201.9	216.5	260.5	112.8	117.1	216.5	98.3	82.0
Turbidity	**(FAU)**	26	22	33	37	43	13	41	95
E. coli	**(CFU/mL)**	0	0	0	0	0	0	0	0
Coliforms	**(CFU/mL)**	0	0	0	0	0	0	0	0
NO_3-N	**(mg/L)**	0.27	0.13	0.17	0.10	0.13	0.07	0.13	0.50
PO_4	**(mg/L)**	0.18	0.08	0.30	<DL	0.15	0.03	0.14	0.42
Na	**(mg/L)**	19.1	20.7	25.5	19.5	4.4	19.7	2.01	2.04
K	**(mg/L)**	8.06	8.45	8.57	8.08	10.9	8.59	5.38	5.34
Mg	**(mg/L)**	4.6	4.83	9.95	4.6	3.75	4.82	2.96	2.87
Ca	**(mg/L)**	12.1	12.9	9.86	12.1	10.2	12.6	10.4	10.1
Cl	**(mg/L)**	5.63	6.00	5.16	5.96	1.86	5.68	0.67	0.85
SO_4	**(mg/L)**	0.25	0.15	0.05	0.22	0.17	0.31	0.05	0.08
HCO_3	**(mg/L)**	0.15	0.16	0.18	0.16	0.09	0.16	0.07	0.08

Controls

Table 3.4 Dry season water quality summary (n=8 except *E. coli* and coliforms n=2)

		Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H
pH		8.75	7.71	9.72	-	9.16	-	-	7.90
DO	**(mg/L)**	10.62	7.17	13.02	-	11.20	-	-	9.96
Temperature	**(ºC)**	17.3	19.3	19.2	-	21.2	-	-	20.0
Conductivity	**(µS/cm)**	238.7	252.3	261.1	-	146.1	-	-	130.3
Turbidity	**(FAU)**	24	12	54	-	55	-	-	91
***E. coli* Count**	**(CFU/mL)**	100	2	103	-	137	-	-	305
Coliform Count	**(CFU/mL)**	0	1	2	-	3	-	-	8
Nitrate	**(mg/L)**	0.40	0.20	0.21	-	0.20	-	-	0.69
Phosphate	**(mg/L)**	0.21	0.12	0.45	-	0.22	-	-	0.42
Na	**(mg/L)**	10.6	9.02	68.5	-	4.6	-	-	2.33
K	**(mg/L)**	1.98	1.79	7.46	-	2.87	-	-	2.34
Mg	**(mg/L)**	2.65	2.44	19.90	-	2.54	-	-	1.65
Ca	**(mg/L)**	1.70	1.54	2.30	-	1.34	-	-	0.72
Cl	**(mg/L)**	1.35	1.20	4.52	-	0.80	-	-	0.58
SO_4	**(mg/L)**	0.45	0.07	0.14	-	0.14	-	-	0.21
HCO_3	**(mg/L)**	0.16	0.15	0.15	-	0.17	-	-	0.10

Controls

3.2.1 pH measurements

Median pH values ranged from pH 6.59 to pH 9. (Figure 3.1). Values of pH were higher in the dry season than in the wet season (p = 0.03). Site G and Site H which were the two control sites (with regard to mine influence) had pH values within the ZW guideline range of pH 6.5 to pH 8.5. All other sampled sites within the Kamativi had pH medians higher than the control sites. Site A, Site C and Site E had pH medians exceeding the upper guideline limit of pH 8.5 during the dry season.

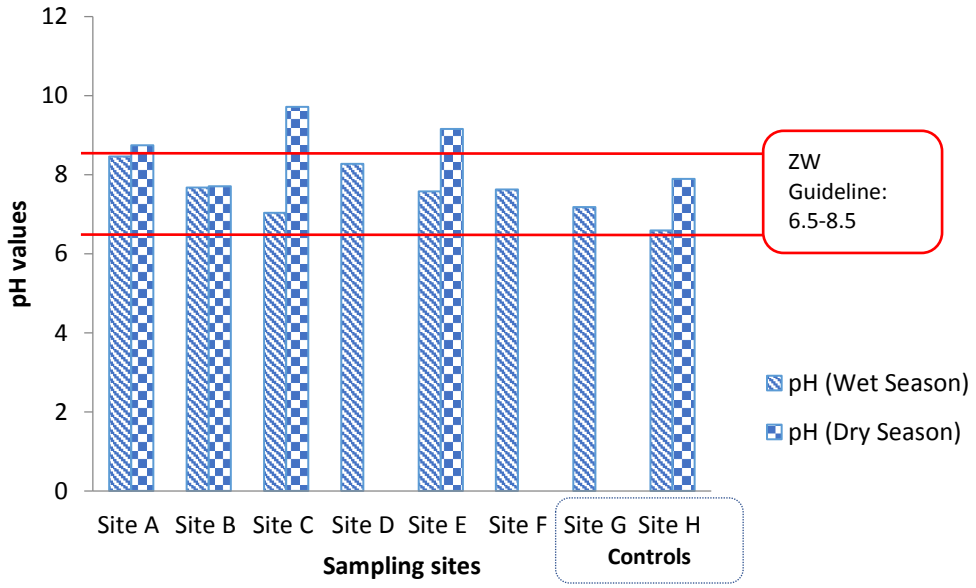

Figure 3.1 pH median values in the wet season (n=3) and dry season (n =8) (ZW=Zimbabwean standard/ Guideline)

3.2.2 Dissolved oxygen measurements

Mean dissolved oxygen (DO) values ranged from 6.51 mg/L to 13.02 mg/L (Figure 3.2). There were no significant differences in dissolved oxygen concentrations between the wet and dry seasons (p = 0.2222). The concentrations of DO were higher in the water within the main Kamativi sampling sites than in the control sites, except for Site B during the dry season and Site C during the wet season

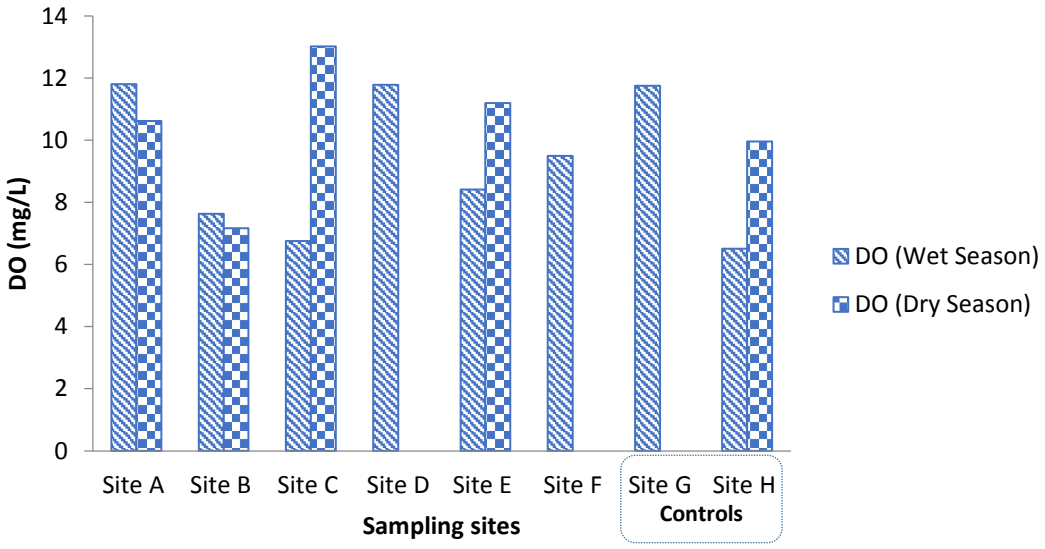

Figure 3.2 Dissolved oxygen (DO) mean concentrations (mg/L) in the wet season (n=3) and dry season (n =8).

3.2.3 Temperature

The wet season was consistently warmer than the dry season (p = 0.007937). Mean temperature values are presented in Figure 3.3. Sites within Kamativi had comparable temperatures to the control sites.

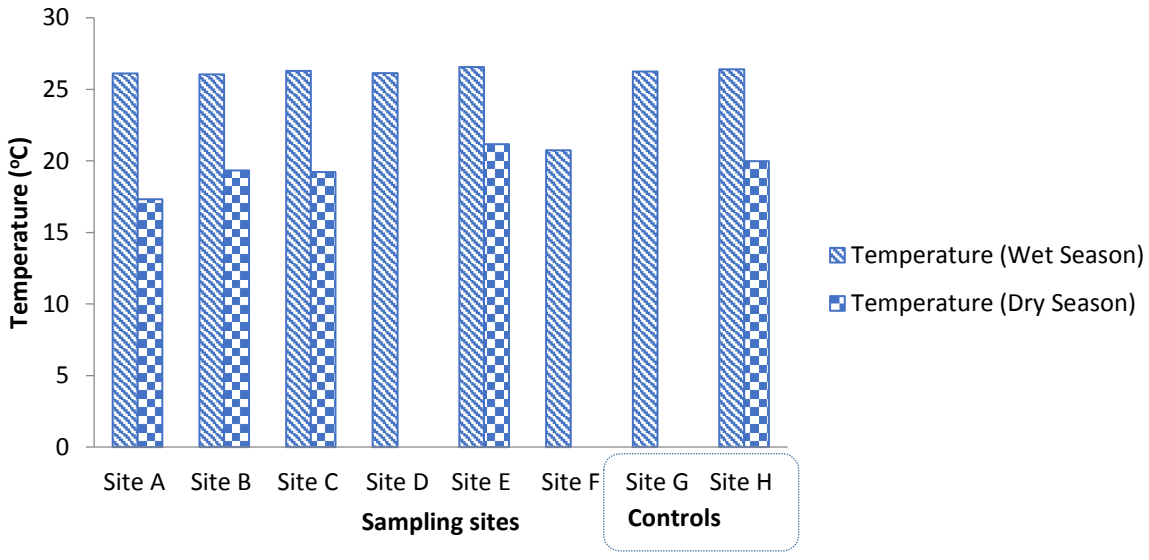

Figure 3.3 Mean values for temperature (^oC) in the wet season (n=3) and dry season (n =8).

3.2.4 Conductivity

Conductivity values ranged from 82 to 261 µS/cm. There was no significant difference between the conductivity of water in the wet season compared to the dry season (p = 0.4206). Sites A, B, and C, which are the closest to the Kamativi mine, were characterised with values higher than those in sites further from the Kamativi mine, including the controls (Figure 3.4). The conductivity of tap water (F) was higher than the source dam (Site A) during the wet season. Control sites G and H, upstream of Kamativi mine, had the lowest conductivity values for both seasons.

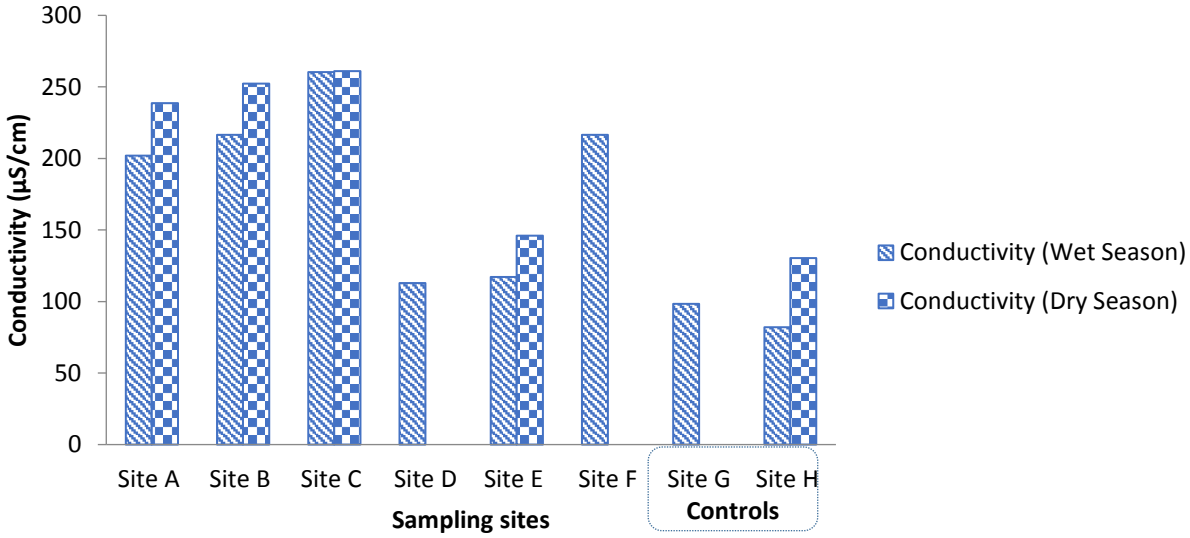

Figure 3.4 Mean conductivity values (µS/cm) in the wet season (n=3) and dry season (n =8).

3.2.5 Turbidity

Water in Kamativi's sampled sites had mean turbidity values ranging from a low of 11.5–95.5 FAU (Figure 3.5). There was no significant difference between the turbidity of water in the wet season compared to the dry season (p = 1). The control Site H had higher turbidity values than water bodies within Kamativi main area and the control river G had higher turbidity than Site D which runs through the town. Distance from the mine did not seem to have an influence on the turbidity of the water bodies. Although there is no strict standard, the tap water turbidity is higher than the stipulated desirable guideline

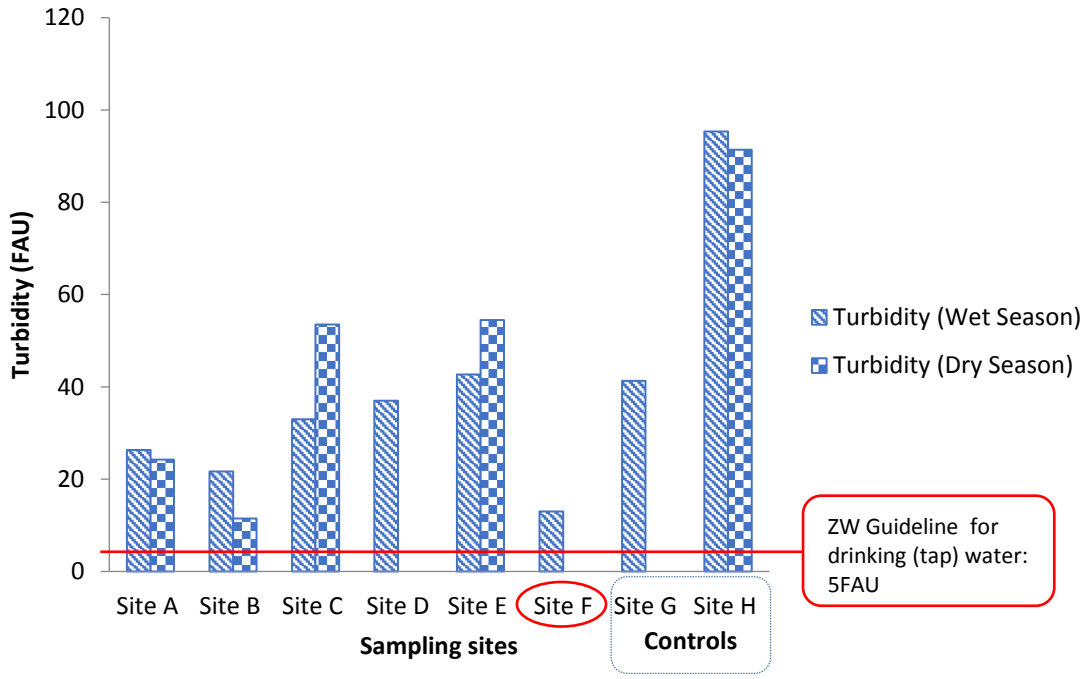

Figure 3.5 Mean turbidity values (FAU) in the wet season (n=3) and dry season (n =8).

3.2.6 Nutrients

Nitrates-Nitrogen (NO_3-N)

NO_3-N concentrations ranged from 0.07mg/L to 0.69 mg/L and phosphates from 0 to 0.45 mg/L. (Figure 3.6) There were no significant difference for the mean NO_3-N concentrations between the wet and dry seasons (p = 0.2933)

Phosphates (PO_4)

PO_4 concentrations were from 0 to 0.45 mg/L (Figure 3.7). There were no significant difference for the mean PO_4 concentrations between the wet and dry seasons (p = 0.4633)

When comparing between similar ecosystems, i.e., lentic and lotic waterbodies on their own, the controls had higher NO_3-N and PO_4 concentrations compared to other sampled sites. The control river G had higher NO_3-N in comparison to the stream Site D which runs through the town. Site H, a control dam had higher nutrient concentrations than all the sites except Site C's PO_4 levels in the dry season. Overall, NO_3-N concentration values were lower in the main Kamativi sampling sites compared with the control Site H.

None of the sampled sites' concentrations exceeded the recommended drinking water guidelines. There was no indication of eutrophication or excessive plant growth in any of the water bodies in Kamativi dams, but there was a sizeable outgrowth of aquatic plants on the surface of Site C in the dry season (observed).

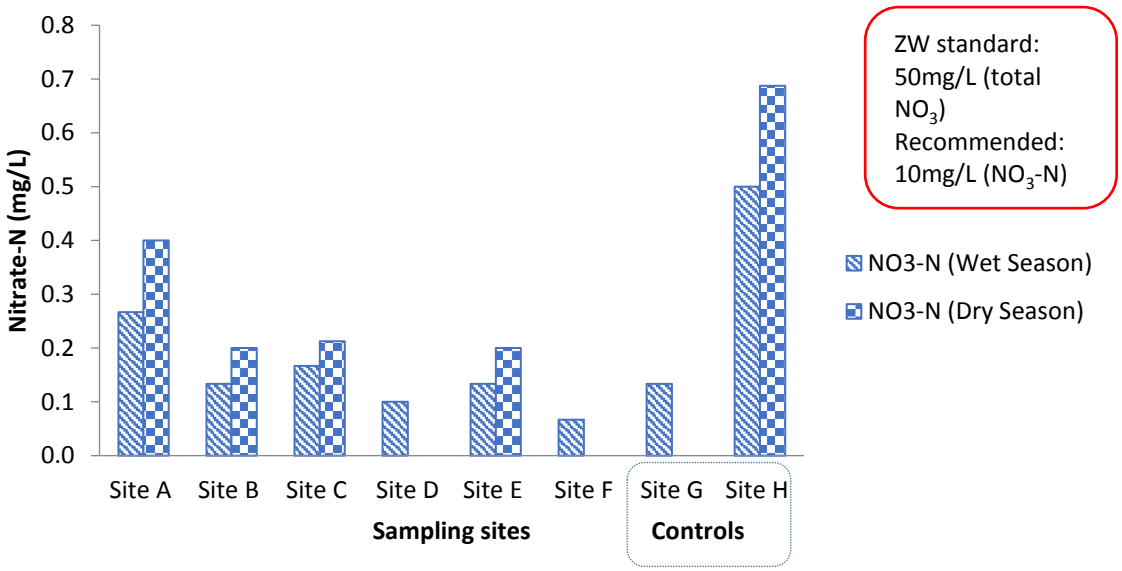

Figure 3.6 Mean values for NO_3-N concentrations (mg/L) in the wet season (n=3) and dry season (n =8).

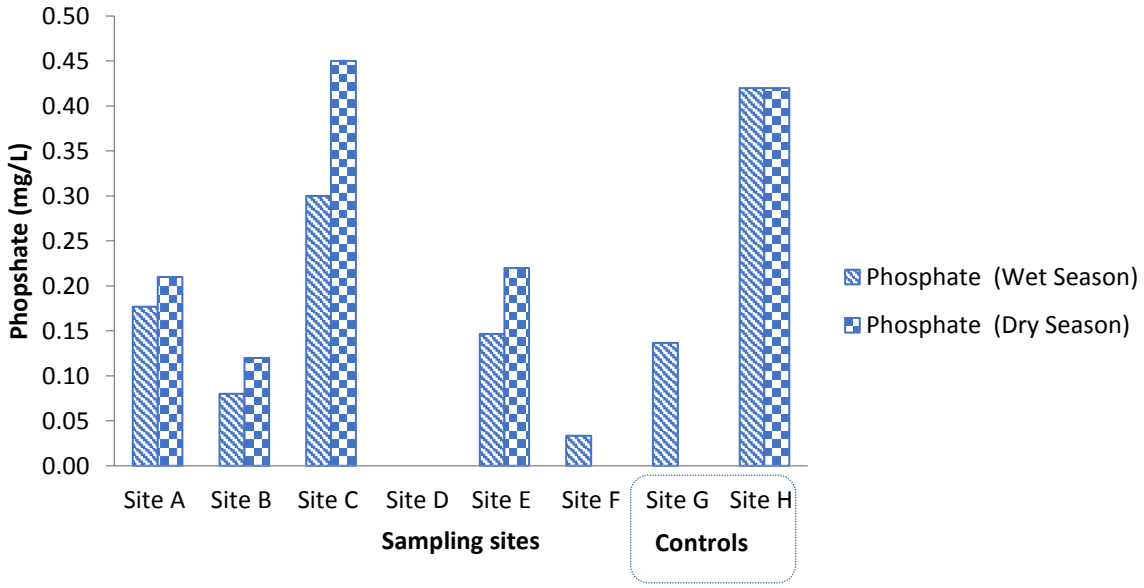

Figure 3.7 Mean values for PO_4 concentrations (mg/L) in the wet season (n=3) and dry season (n =8).

3.2.7 Faecal bacteria

Faecal bacteria counts ranged from 0 to over 300 colony-forming units/mL (CFU/ml). There was a significant difference in both the *E. coli* and coliform bacteria populations between the wet and dry seasons (for *E. coli*, $p = 0.0075$ and for coliforms, $p = 0.0254$). Results for the wet season count were all zero (CFU/mL); however, there was a high faecal bacteria count in 4 out of the 5 sites sampled in the dry season (Figures 3.8 and 3.9). Colony count increased with distance from the mine.

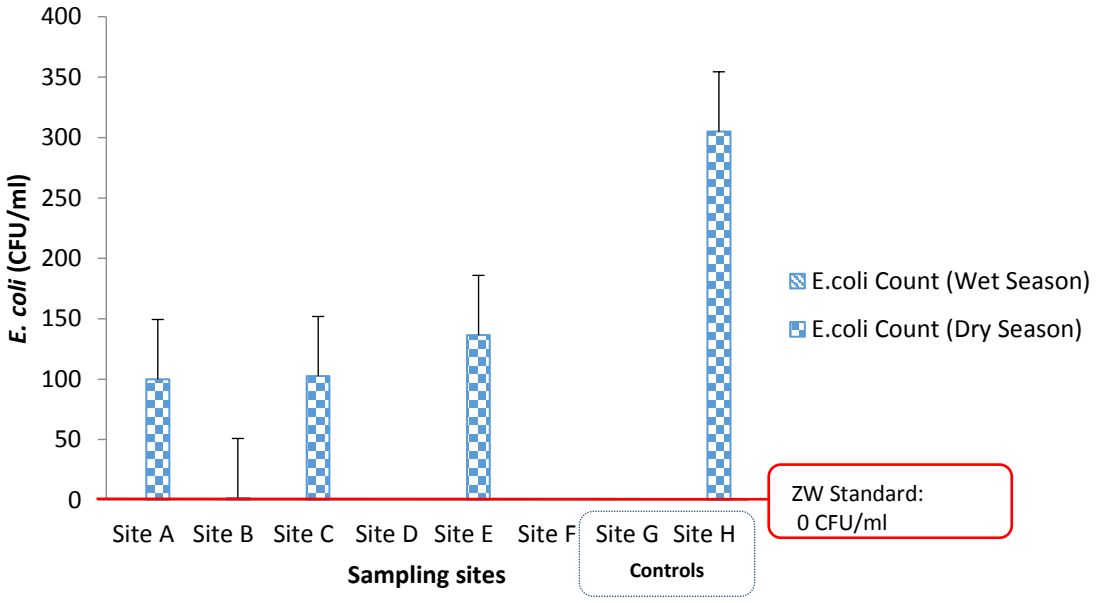

Figure 3.8 E. coli (CFU/mL) in the wet season (n=2) and dry season (n =2).

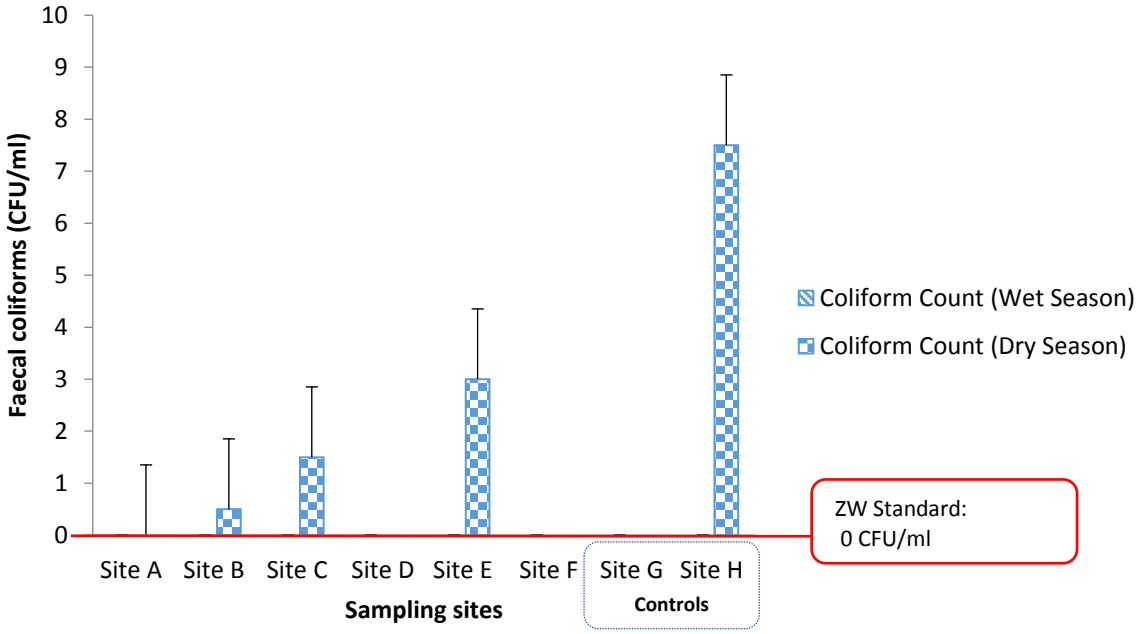

Figure 3.9 Faecal coliform results (CFU/mL) in the wet season (n=2) and dry season (n =2).

3.2.8 Major ions

Cations

Ca^{2+} concentrations were from 0.72 to 12.6 mg/L and were higher in the wet season than in the dry season (p = 0.007937). K^{+} concentrations ranged from 1.79 to 10.9 mg/L and were higher in the wet season than in the dry season (p= 0.01587). Mg^{2+} concentrations were from 1.65 to 19.9 mg/L and there was no significant difference between the wet and dry season (p = 0.1508). Na^{+} concentrations ranged from 2.01 to 68.5 mg/L. There was no significant difference between the wet and dry season (p=1)

In site-by-site comparisons, Na^{+} levels were higher in the central Kamativi samples compared to the controls G and H. Site C had the highest Na^{+} concentration of 68.5mg/L. Site E was the exception to this trend (Figure 3.10 and 3.11). K^{+}, Mg^{2+} and Ca^{2+} concentrations were comparable between the controls and sampled sites.

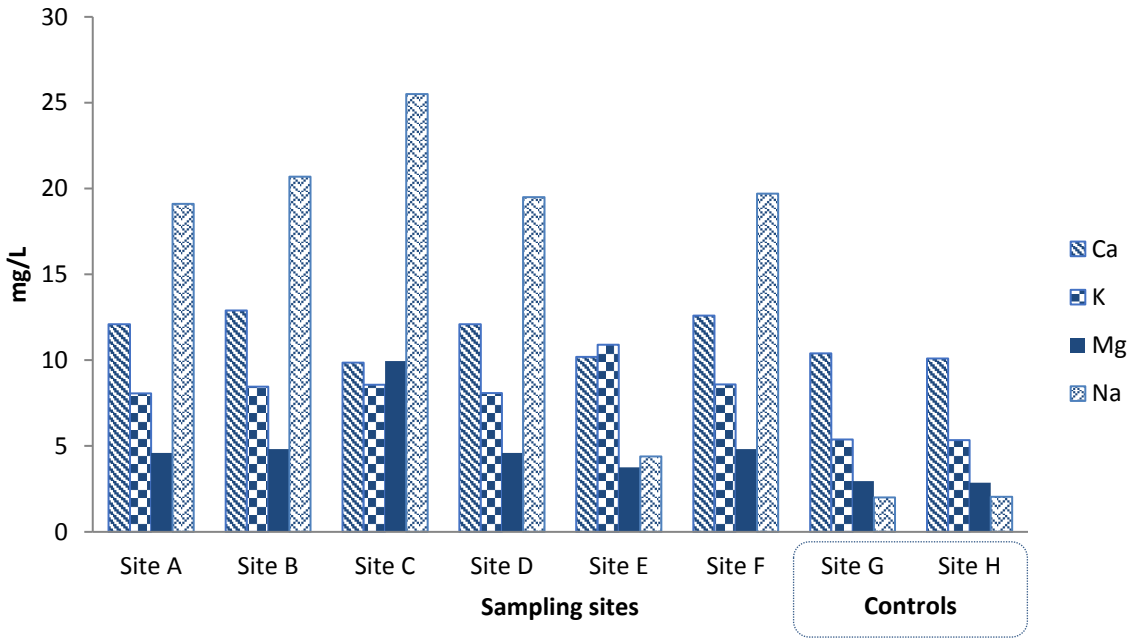

Figure 3.10 Concentration of major cations (mg/L) in the wet season (n=3)

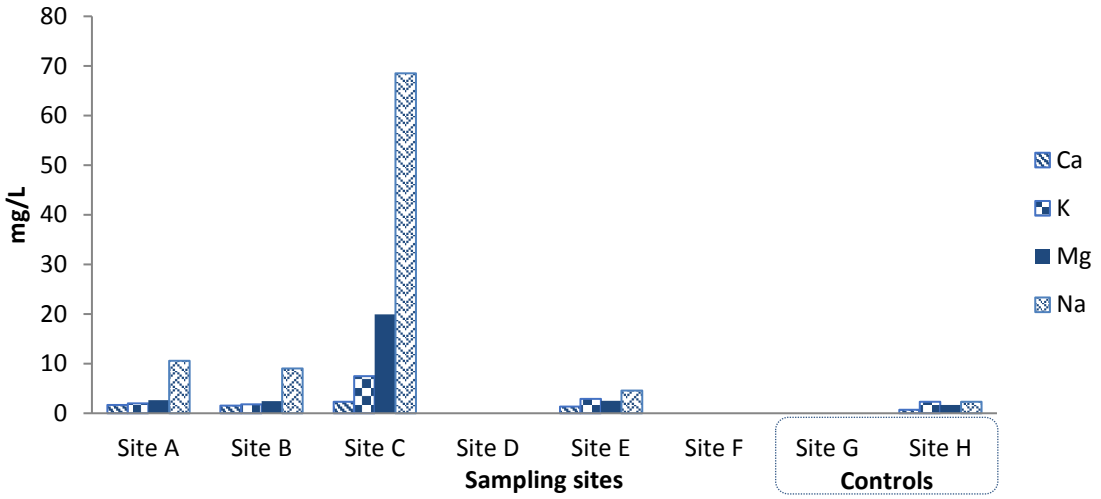

Figure 3.11 Concentration of major cations (mg/L) in the dry season (n=8)

Anions

Cl^- concentrations ranged from 0.58 to 6 mg/L. There was no significant difference in concentrations between the wet and dry seasons (p=0.09524). HCO_3^- concentration ranged from 0.07 to 0.18 mg/L with no significant difference between the wet and dry seasons (p=0.6905). SO_4^{2-} concentrations were from 0.07 to 0.31 mg/L and there was no significant seasonal difference (p=0.8413)

In site-by-site comparisons, Cl^- concentrations were the highest among the 3 anions across all sites. SO_4^{2-} and HCO_3^- concentrations were comparable across sites. The concentration of Cl^- was higher in inner Kamativi sampled sites compared with controls, Site C being the highest.

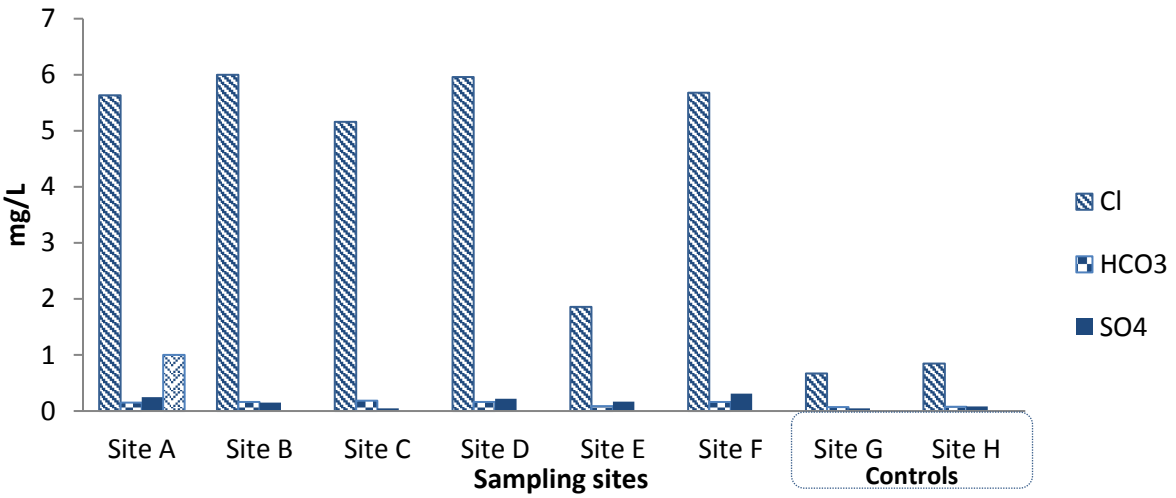

Figure 3.12 Concentrations of major water anions in the wet season (n=3)

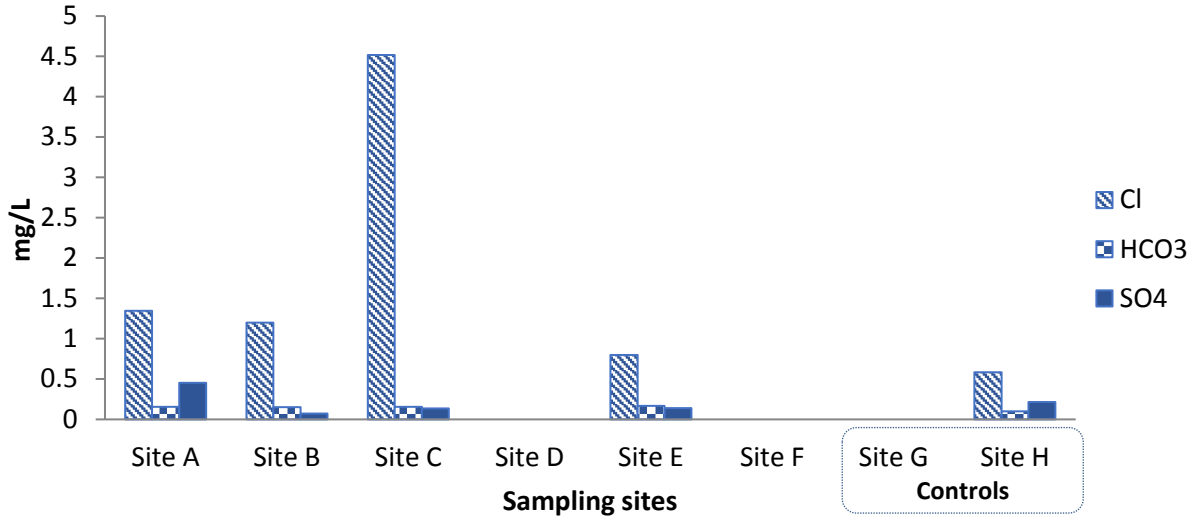

Figure 3.13 Concentration of major water anions (mg/L) in the dry season (n=8).

3.3 Trace elements

There was a wide range of trace element concentrations ranging between < 0.1 and 2360 µg/L. Most trace elements were below ZW standards/WHO health-based guidelines for drinking water quality, except for arsenic, and isolated high levels of aluminium (Site C) and manganese (Site H). Some elements were detected in a semiquantitative ICP MS scan, but proved to be below detection limit in a full, quantitative ICP MS scan. Those trace elements with concentrations below the detection limits are included in Appendices 3 to 7. Summary trace element results are presented in Tables 3.5 to 3.8. Tin (Sn) was consistently below detection limit (0.1µg/L), which was unexpected given that Kamativi is mainly a tin mine. A discussion on tin is in the next chapter. The elements below are presented in alphabetical order.

Table 3.5 Detectible total HNO_3 acid-soluble trace element concentrations summary in the wet season (n=1)

		Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H
Al	(µg/L)	12	19	273	16.3	86.4	30	12.8	9.51
As	(µg/L)	18.10	23.30	47.50	17.30	3.67	17.00	2.95	3.05
Cu	(µg/L)	3.81	1.51	4.49	2.06	1.61	2.20	1.70	0.96
Fe	(µg/L)	207	213	781	199	444	166	101	163
Li	(µg/L)	2110	2280	2030	2030	114	2240	47.2	25.8
Mn	(µg/L)	119	309	281	114	291	99.6	72.6	206
Nb	(µg/L)	0.07	0.06	0.08	0.04	0.03	0.03	0.02	0.02
Pb	(µg/L)	0.27	0.32	2.66	0.27	1.04	0.66	0.25	0.23
Ta	(µg/L)	0.21	0.19	0.26	0.16	0.15	0.15	0.13	0.12
W	(µg/L)	31.10	125.00	2.68	68.30	1.72	1.00	0.57	0.39
Zn	(µg/L)	3.49	13.70	5.84	5.06	4.71	15.90	6.56	6.17

Controls

Table 3.6 Detectible total HNO_3 acid-soluble trace element concentrations summary in the dry season (n=1) .Sites D, F and G were unavailable for sampling during the dry season

	Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H
Al (µg/L)	8.58	2.83	41.40	-	13.20	-	-	175.00
As (µg/L)	13.50	16.80	35.70	-	2.20	-	-	3.54
Cu (µg/L)	0.96	0.63	3.28	-	0.98	-	-	3.50
Fe (µg/L)	159.00	38.10	140.00	-	194.00	-	-	813.00
Li (µg/L)	2050.00	2080.00	2150.00	-	93.70	-	-	3.28
Mn (µg/L)	206.00	66.30	101.00	-	288.00	-	-	1050.00
Pb (µg/L)	0.15	0.17	0.43	-	0.34	-	-	4.04
Ta (µg/L)	0.10	<0.1	0.10	-	<0.1	-	-	<0.1
W (µg/L)	0.10	0.10	0.32	-	<0.1	-	-	<0.1
Zn (µg/L)	1.34	0.95	1.95	-	1.37	-	-	5.47
							Controls	

Table 3.7 Detectable dissolved trace element concentrations summary in the wet season (n=1)

	Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H
Al (µg/L)	5.04	11.2	7.42	4.55	4.95	5.3	4.68	3.5
As (µg/L)	15	17.4	30.6	16	2.31	15	2.74	2.53
Cu (µg/L)	1.76	3.74	1.9	3.12	1.29	1.59	1.24	2.67
Fe (µg/L)	3.09	19.2	2.82	1.48	4.71	3.94	3.63	2.02
Li (µg/L)	2150	2360	2010	2250	124	2230	49.2	36.4
Mn (µg/L)	0.83	0.73	0.53	0.21	0.33	0.56	0.65	0.34
Nb (µg/L)	0.94	0.69	0.54	0.29	0.22	0.16	0.12	0.08
Pb (µg/L)	0.67	0.55	0.35	0.23	0.24	0.11	0.09	0.05
Ta (µg/L)	0.97	0.76	0.76	0.44	0.35	0.31	0.26	0.22
W (µg/L)	0.87	0.71	0.79	0.37	0.13	0.20	0.06	0.02
Zn (µg/L)	7.96	10.7	8.06	9.18	1.34	6.54	4.11	5.13
							Controls	

Table 3.8 Detectable dissolved trace element concentrations summary in the dry season (n=1). Sites D, F and G were unavailable during the dry season

	Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H
Al (µg/L)	1.34	0.94	6.81		1.18			1.56
As (µg/L)	3.64	3.68	36.70		1.02			1.25
Cu (µg/L)	0.83	0.55	2.43		1.06			1.13
Fe (µg/L)	2.80	0.96	21.90		1.30			5.59
Li (µg/L)	416	371	2100		102			42
Mn (µg/L)	46.70	3.46	0.63		0.41			71.60
Pb (µg/L)	0.01	0.01	0.24		0.01			0.01
Ta (µg/L)	0.27	0.18	0.21		0.12			0.10
W (µg/L)	0.10	0.08	0.56		0.06			0.04
Zn (µg/L)	1.22	1.59	1.40		1.03			2.12
							Controls	

3.3.1 Aluminium (Al)

Total (acid soluble) Al concentrations ranged from 9.51 to 273 µg/L and dissolved concentrations from 1.18 to 11.2 µg/L (Figure 3.14). There was no evidence of mine proximity effect on the concentrations of aluminium in the water bodies. Site C (disused quarry dam) had an isolated high concentration of total acid (HNO_3) soluble Al in the wet season, and the total exceeded the WHO maximum guideline of 0.2 mg/L (Figure 3.14). The control Site H also showed an isolated peak in the dry season that was, however, below the WHO guideline. The rest of the sites had consistently low values in comparison with the guideline. There was no significant difference in the concentration of either total HNO_3 soluble or water soluble (dissolved) aluminium between the dry and wet seasons. (Total Al: $p = 0.5476$) (Dissolved Al: $p = 0.05556$).

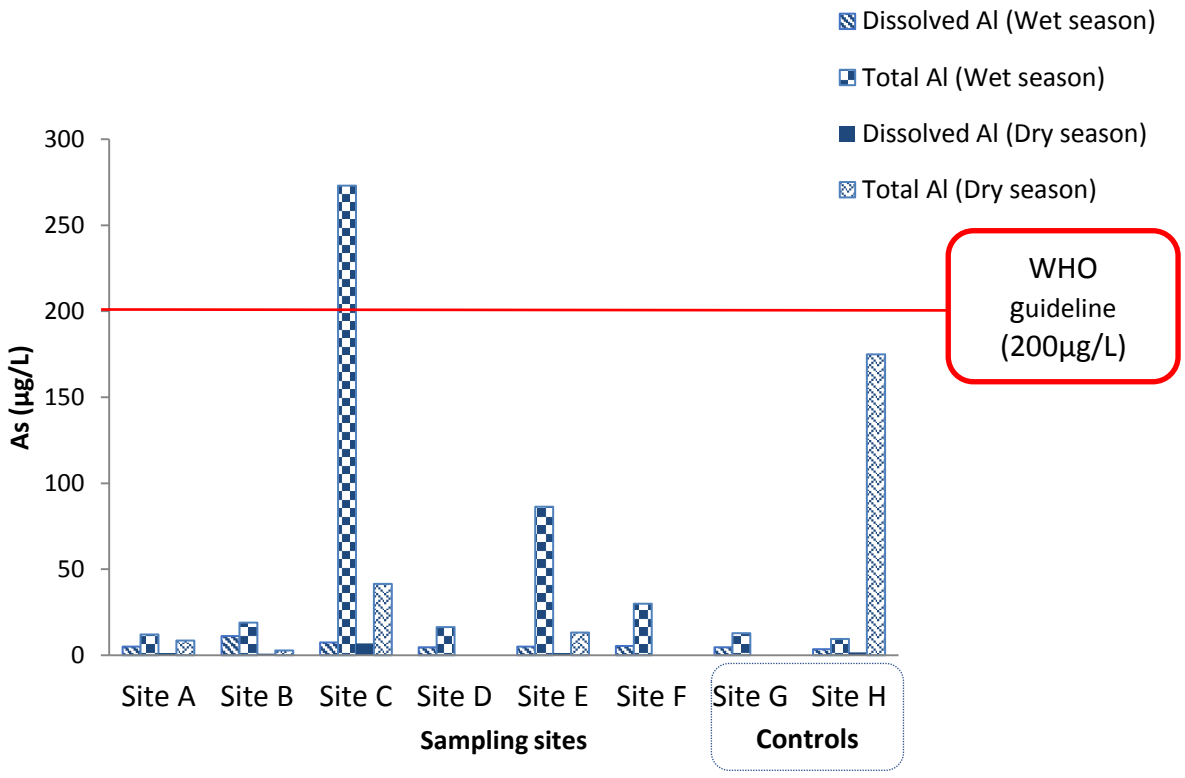

Figure 3.14 Concentration of Al (µg/L) in the wet season and dry season (n=1).

3.3.2 Arsenic (As)

Concentrations for total arsenic ranged from 2.2 µg/L to 47.50 µg/L while dissolved concentrations were between 1.02 µg/L to 36.7 µg/L. In 5 out of 6 main sources of water in Kamativi (excluding the controls), arsenic was present in concentrations exceeding the ZW standard limit of 0.01mg/L (10µg/L), which is also the WHO health-based guideline limit for drinking water (Figure 3.15). Concentrations increased with proximity to the mine, with Site C (former opencast quarry) having the highest concentrations, while Site E had the lowest concentrations and were comparable to the two control sites. Tap water (reticulated from Site A and Site B) had comparable levels to Site A and Site B, which are within a 3 km radius of the main mining grounds. Site D, which runs through the mining area, also had elevated levels of arsenic. Kamativi water bodies had higher concentrations than the two control sites in both seasons, except for Site E (about 7.5 km to the north of the mining area). There was no significant difference in the concentration of total acid (HNO_3) soluble and water-dissolved arsenic between the wet and dry seasons (for both total and dissolved arsenic: p = 0.5476).

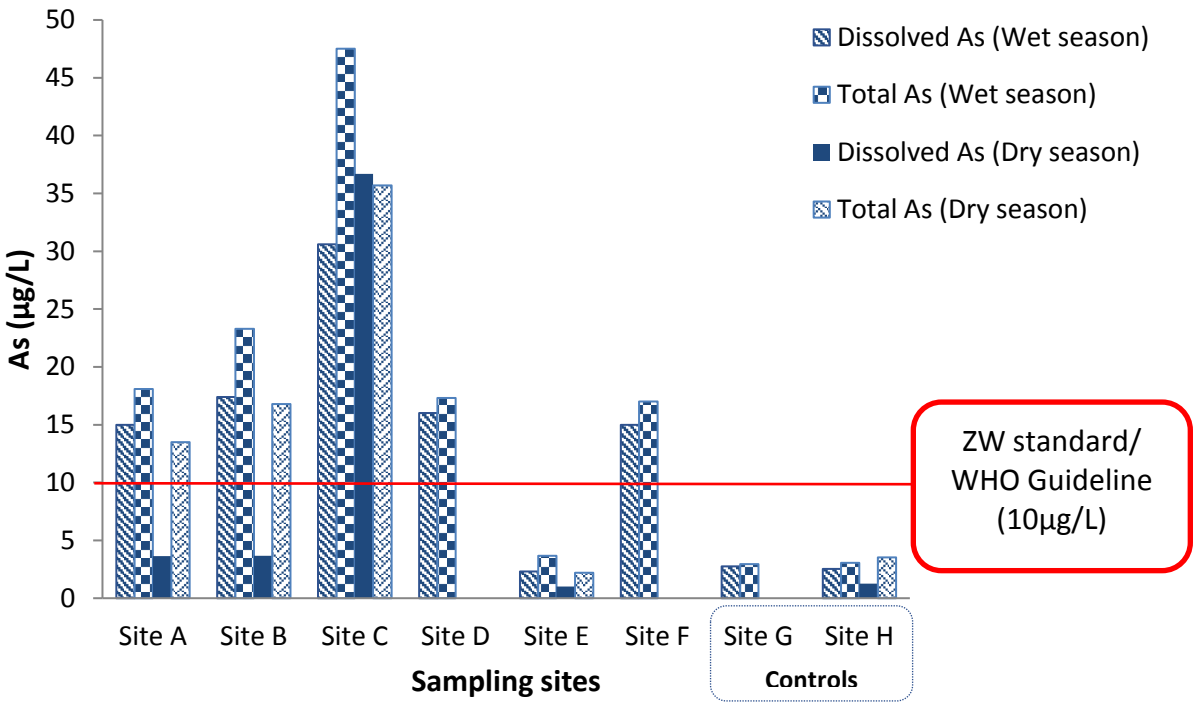

Figure 3.15 Concentrations of As (µg/L) in the wet season and dry season (n=1)

3.3.3 Copper (Cu)

Total (acid soluble) copper (Cu) concentrations ranged from 0.63 µg/L to 4.49 µg/L and water-dissolved concentrations from 0.55 µg/L to 3.74 µg/L. None of the sites exceeded the ZW standard limit of 2 mg/L (2,000 µg/L). Site C had the highest concentration of Cu in the wet season. However, all values from sampled sites were comparable to the controls (Figure 3.16). The proximity to the mine did not appear to have an influence on the concentrations.

There was no significant difference in the concentrations of both total acid (HNO_3) soluble Cu (p = 0.3095) and dissolved Cu (p = 0.5556) between the dry and the wet seasons

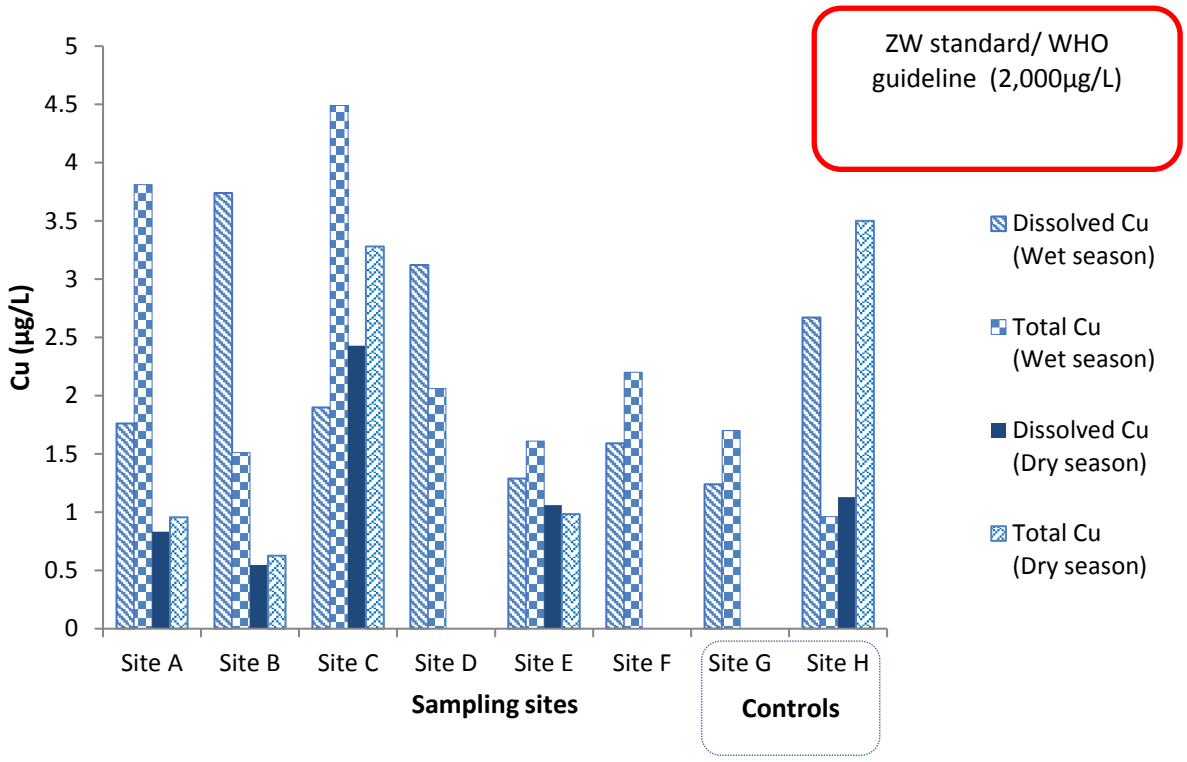

Figure 3.16 Concentration of Cu (µg/L) in the wet season and dry season (n=1).

3.3.4 Lithium (Li)

Total lithium (Li) concentrations ranged from 3.28 µg/L to 2,280 µg/L. Dissolved concentrations were from 42 µg/L to 2,360 µg/L (Figure 3.17). Although not included in ZW standards/WHO guidelines, Li concentrations were very high in comparison to other trace

elements. Lithium concentrations were highest in the water bodies within a 3 km radius or with a direct link with the mining grounds. Generally, lithium concentrations increased with proximity to the mine. The two control sites G and H both had much lower concentrations of Li compared to the rest of the sampled sites, except Site E which had relatively low values too.

There was no significant difference in the concentrations of both total acid (HNO_3) soluble Li (p = 0.6905) and dissolved Li (p = 0.5476) between the wet and dry seasons

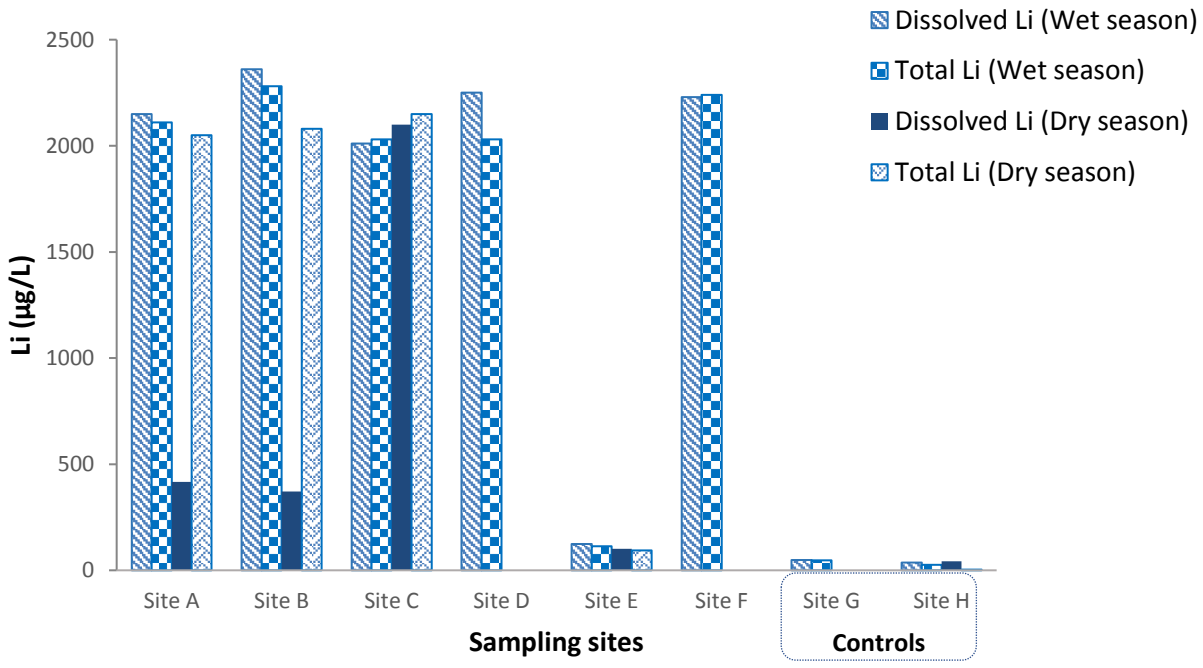

Figure 3.17 Li concentrations (µg/L) at sites A-H in the wet season (n=1) and dry season (n=1).

3.3.5 Iron (Fe)

Total HNO_3 acid soluble Fe concentrations had a wide range, from 38.1 µg/L to 813 µg/L. Dissolved concentrations were from 0.96 µg/L to 19.2 µg/L. Site C had the highest peak concentration of Fe in the wet season while a control Site H had the highest Fe in the dry season. However, most values from sampled sites were comparable to the controls (Figure 3.18). The proximity to the mine did not appear to have an influence on the Fe

concentrations. There was no significant difference in the concentrations of both total acid (HNO_3) soluble Fe (p = 0.2222) and dissolved Fe (p = 0.6905) between the dry and the wet seasons

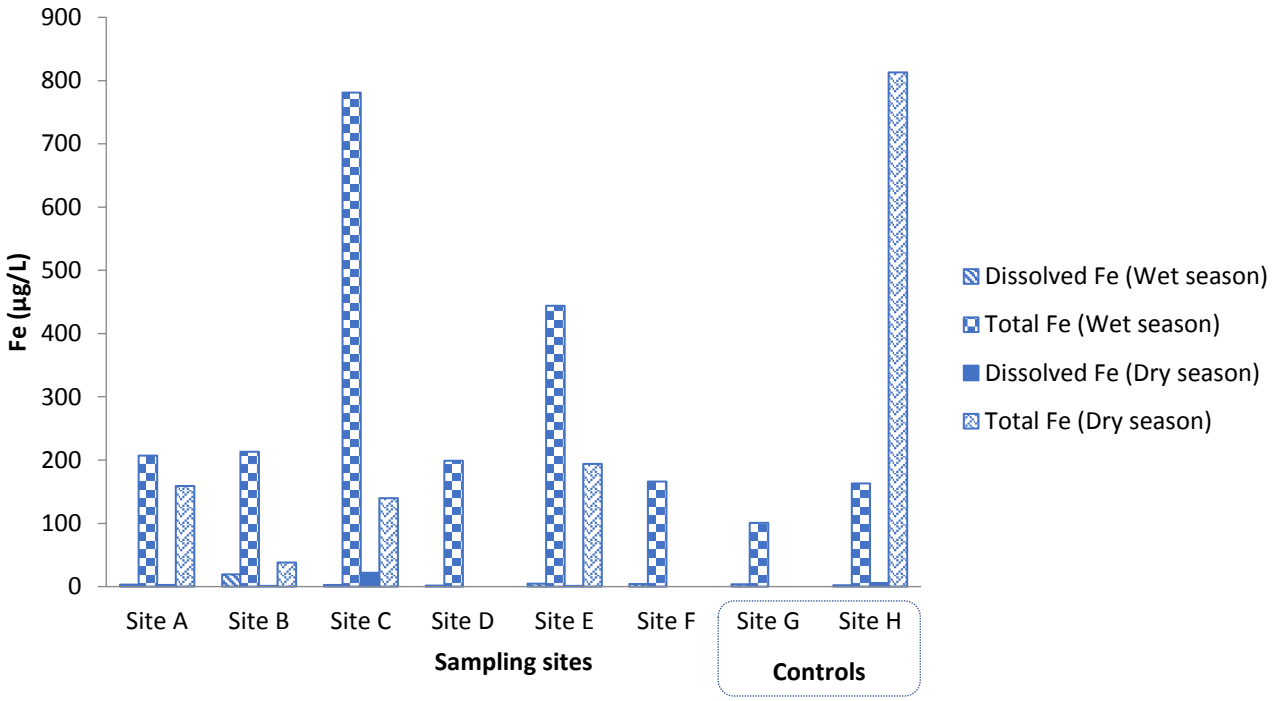

Figure 3.18 Concentration of Fe (µg/L) in the samples collected in the wet season and dry seasons (n=1)

3.3.6 Manganese (Mn)

Total HNO_3 soluble Mn concentrations ranged from 66.3 µg/L to 1,050 µg/L while dissolved concentration ranged from 0.41 µg/L to 71.6 µg/L. The values for all six main Kamativi water bodies (excluding the controls) were generally below the ZW guideline limit. A control Site H had an isolated case of high Mn concentration (in the dry season only) that exceeded the stipulated guideline by over 50%. The other control Site G (only able to be sampled in the wet season) had both total and dissolved manganese concentrations below the limit and its values were comparable to other sampled sites. Proximity to the mine had no evident impact on the Mn concentrations. There was no significant difference in concentrations of both total acid (HNO_3) soluble (p = 0.6004) and dissolved Mn (p = 0.1508) between the wet and dry seasons.

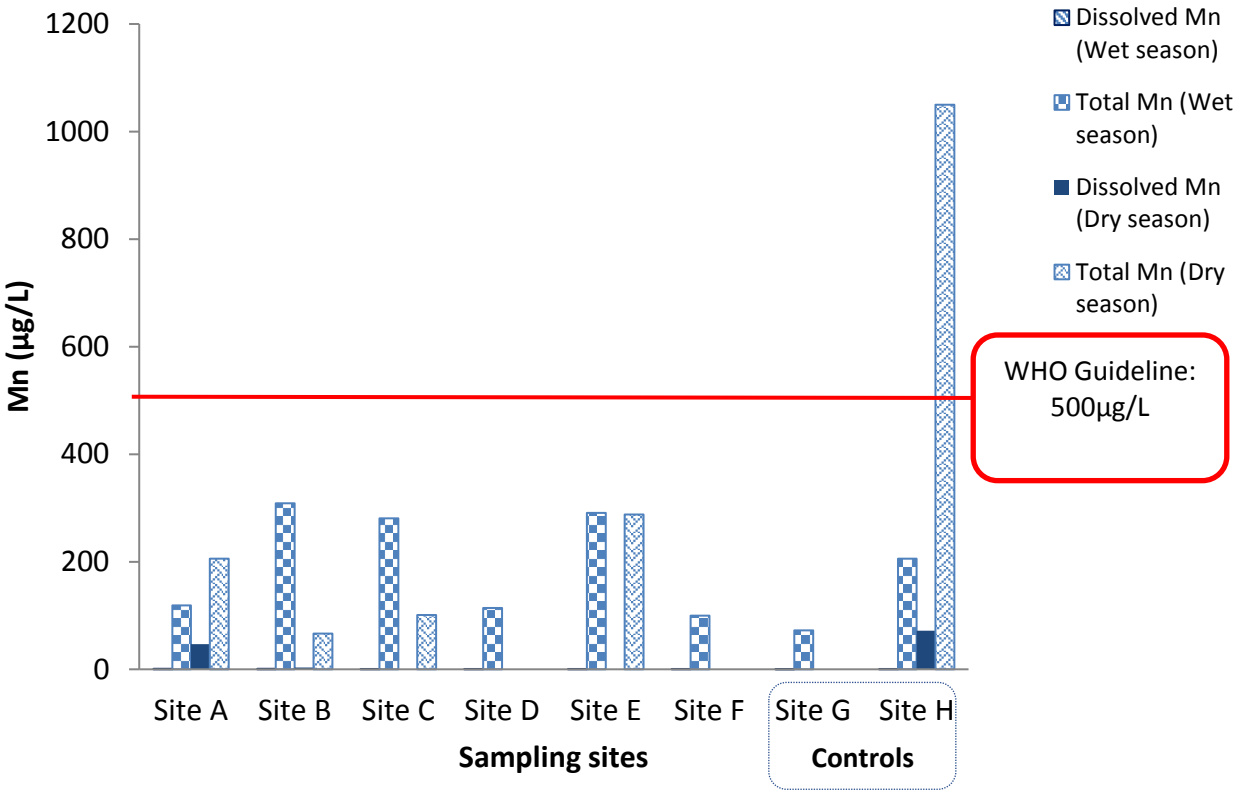

Figure 3.19 Concentration of Mn (µg/L) in the samples collected in the wet season and dry seasons (n=1).

3.3.7 Lead (Pb)

Total lead (Pb) concentrations ranged from 0.15 µg/L to 4.04 µg/L and dissolved Pb ranged from 0.01 µg/L to 0.67 µg/L. None of the sites exceeded the standard limit of 10 µg/L (0.01 mg/L). All six main Kamativi water bodies (excluding controls) had low concentrations, with a peak of 2.66 µg/L for Site C's total Pb in the wet season. This was lower than the control Site H which had an isolated peak of 4.04 µg/L in total Pb concentration in the dry season. Proximity to the mine did not appear to be an influencing factor on the concentration of Pb in the water bodies. Sites C, E and F, as well as the control Sites G and H had higher total acid (HNO_3) soluble Pb concentrations than dissolved Pb (Figure 3.20).

There were significantly higher dissolved Pb concentrations in the wet season than in the dry season (p = 0.01587). However, there was no significant difference in the concentration of total acid (HNO_3) soluble Pb between the wet and dry seasons (total Pb: p =0.8413).

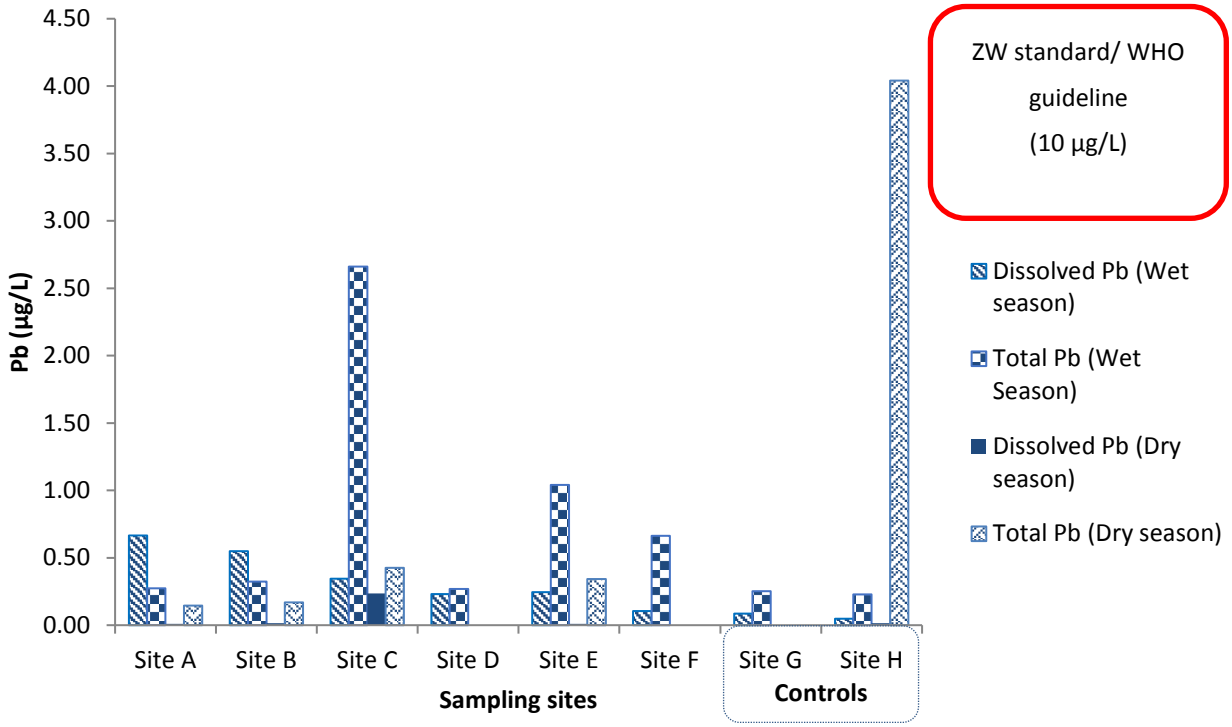

Figure 3.20 Concentration of Pb (µg/L) in the wet season and dry seasons (n=1)

3.3.8 Zinc (Zn)

The total zinc (Zn) concentrations ranged from 0.95 µg/L to 15.9 µg/L and dissolved concentrations were from 1.03 µg/L to 10.7 µg/L (Figure 3.21). Proximity to the mine did not appear to be an influencing factor on the concentrations of Zn. None of the sites exceeded the WHO health-based guideline of 3,000 µg/L (3 mg/L). Tap water (Site F) contained the highest concentration of total acid (HNO_3) soluble Zn, and the concentration was higher than reservoir sources Site A and Site B. There was a significant difference in the concentration of total acid (HNO3) soluble Zn in the wet and dry seasons (total Zn: p= 0.03175), i.e. total Zn

levels were higher in the wet season than in the dry season, but for dissolved Zn (p = 0.05556), there was no significant difference between the two seasons.

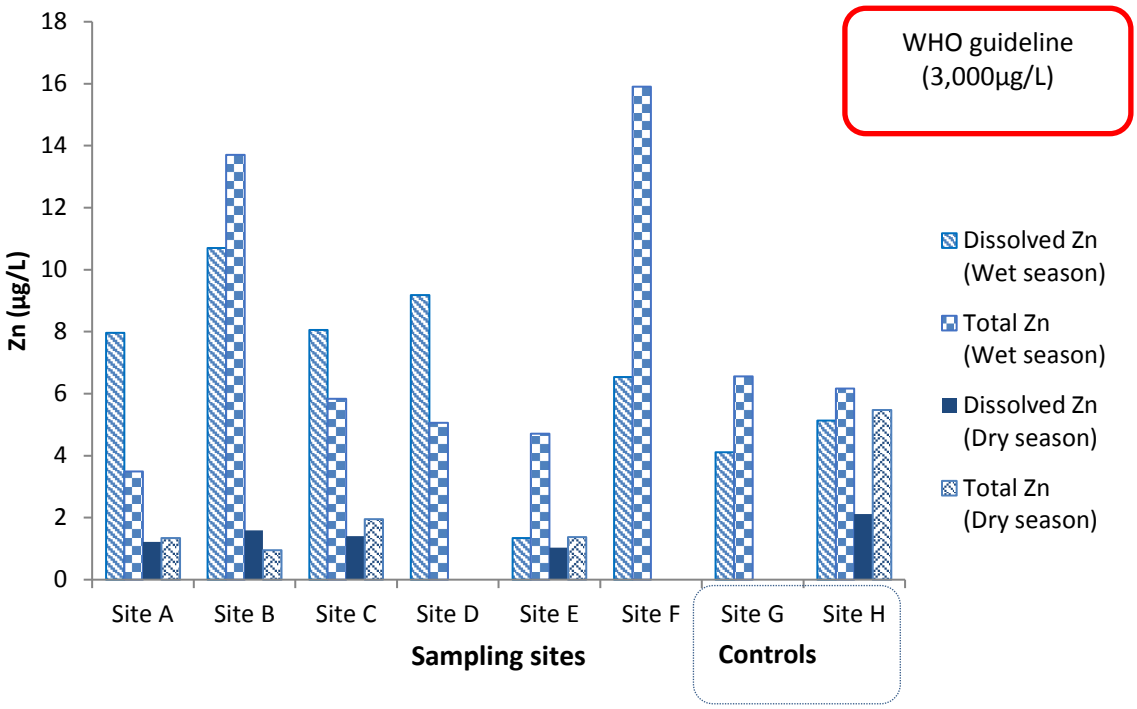

Figure 3.21 Concentration of Zn in the wet and dry season samples. (n=1)

4.0 DISCUSSION

4.1 Identification and quantification summary

Kamativi water bodies assessed from samples collected in the wet and dry seasons of 2016 presented some health and aesthetic concerns regarding the suitability of the water for the purposes of human consumption, as well as compliance with Zimbabwean (ZW) standards and guidelines. Some parameters stood out as noncompliant with the requirements of the ZW standards and WHO health-based guidelines for drinking water – these include the water quality parameters of pH, turbidity, and microbiological content. Arsenic stood out as a trace elements of concern in Kamativi, with a clear and consistent concentration above the ZW standard limit. Table 4.1 presents a summary of parameters where standards and guidelines were not met on at least one occasion.

Table 4.1 Summary of parameters and sites of concern in Kamativi during the wet and dry season of 2016.

Parameter	Sites Concerned	Comment
pH	Site A, Site C, Site E	Results exceeded the upper recommended limit of pH 8.5 during the dry season.
Turbidity	Site F	Results exceeded the recommended limit of 5 FAU for tap water. Current treatment regime not effectively reducing the turbidity of raw water.
E. coli & coliforms	Site A, Site C, Site E, Site H	There is evidence of faecal contamination and likelihood of presence of pathogenic microorganisms in the water.
Al	Site C	The site had an isolated peak of total Al concentration in the wet season that exceeded the WHO guideline limit.
As	Site A, Site B, Site C, Site D, Site F	Arsenic concentrations at the sites exceeded the ZW standard limit.
Li	Site A, Site B, Site C, Site D, Site F	Not regulated but was present in high concentrations in comparison to all other trace elements.
Mn	Site H	Mn was not of concern in main Kamativi water bodies; however, a control site H had an isolated high concentration in the dry season that exceeded the WHO guideline.

4.1.1 Spatial distribution of pollutants

Most trace elements presented in the previous chapter show higher concentrations in the water bodies closer to the mine than in those far from it. The trend was similar for those parameters of concern discussed in this chapter (Table 4.1). Site A and Site B are very close to the mining areas, as they were built specifically to supply the mine with water for operations (Figure 4.1). Site C is a former opencast quarry site with exposed inner rock surfaces. Arsenic and Li concentrations discussed above attest to higher concentration in the sites shaded in yellow in Figure 4.1.

The east wing of the main Kamativi dam (Site A), being the main reservoir for tap water delivery, is the most important water body in Kamativi and yet is part of the area with high concentration of arsenic. Lack of ongoing monitoring and reliable treatment makes the quality of raw water at Site A representative of what residents are drinking from the taps. Site F was a randomly selected tap from the main Kamativi residential area.

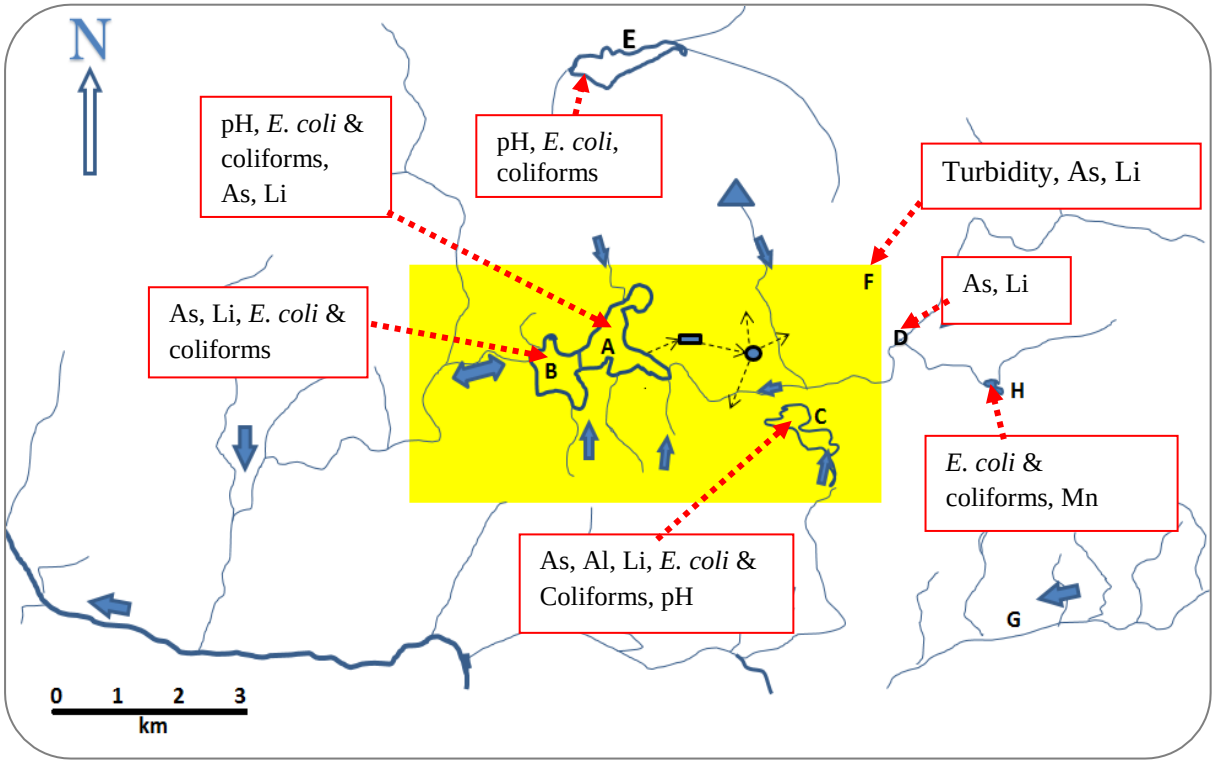

Figure 4.1 Parameters with abnormal values in relation to geographical location in Kamativi. The area close to the mining area (shaded in yellow) had higher concentration of trace elements compared to areas further away.

Comparing the six main sites (A–F) that are used as domestic water sources with an additional two control sites (G and H) in the greater Kamativi area (which are not in the path of flow of water from the mining grounds), revealed a trend in the analysis graphs of particulate vs dissolved trace element concentrations (Figures 4.3 to 4.6) in which concentrations were generally higher in sites close and downstream to the main Kamativi mining area (see Figures 2.1 and 4.1). Kamativi main dam (Site A and Site B), lie in a valley region that receives inflows from the close mining grounds on its south and south-eastern shores as well as from low density residential areas on the northern side of the dam (Figure 2.1) Site C is close by and accepts partial flow from smaller streams that are interconnected and run along with Syabunyangu stream (Site D) on a limited scale during the wet season. Higher trace element concentrations in waters immediately downstream of mining areas are not unique to Kamativi. Nimick et al (2004) established that some metals, including As, Pb and Zn tended to have concentrations higher than usual in areas downstream of inactive mine sites for data collected over a period of 4 years (1996 – 2000) in Montana, United States. Water flow down the hills into the river valleys, and from the wider catchment area, enhance this transportation of metals to a lower zone where they become concentrated or accumulate (Nimick et al, 2004). The strong correlation between mine-related trace elements such as Li and toxic levels of arsenic (Table 4.3) further validates the conclusion that the mine has a polluting influence on the Kamativi water.

4.2 Physico-chemical and microbiological implications

Values for pH, *E.coli*, and faecal coliforms differed significantly between the two seasons, as presented in Chapter 3. The upper limit for pH was exceeded in at least three sites during the dry season. *E.coli* and coliform bacteria amounts were well above the limit in the dry season.

4.2.1 Implications of basic pH on the water quality

The pH value is usually considered to have only an aesthetic impact (USEPA, 2014) on drinking water, although the recommended range is pH 6.5–8.5. The actual pH of water is an outcome of varied interactions of chemical elements and biological processes within it. Elevated pH levels, like those seen in some Kamativi waters, may result in a bitter taste in drinking water; reticulation pipes and water housing chambers may also be encrusted with layers of salt precipitates (Tucker & D'Abramo, 2008; Grey, 2008). This can also suppress the effectiveness of disinfection using chlorine. A higher dosage of chlorine than normal

would be required under high pH conditions. High pH can also aid solubility of metals, potentially increasing the concentration of toxic metals in water. The main implication of abnormal pH, therefore, is to indicate poor water quality that warrants further investigation of underlying causes. The higher pH in the dry season is likely a result of a reduction in the water volume in most water bodies, thereby increasing the concentration of salts and hence hydroxyl ions (OH^-), which positively influenced the pH in the dry season (Tucker & D'Abramo, 2008). Although no actual measurements of water volume were taken, the water was evidently less in the dry season, with two of the sampling sites having dried out already.

High pH, to a small extent, could also reflect the fact that sampling was done during the day. Ideally, pH in a fresh water environment rises in the daytime when carbon dioxide is reduced by photosynthetic aquatic and riparian plants. Conversely, the pH falls during the night due to carbon dioxide addition to the water through respiration (Tucker and D'Abramo, 2008). Kamativi has some carbonate-containing minerals, e.g., zabuyelite (Li_2CO_3) which is a major form of lithium-containing ore (Thomson's publications, 1984). These carbonate-containing rocks likely increase the alkalinity of water, thereby aiding its buffering capability, which keeps the pH close to neutral. Additional carbonate amounts can result in neutral water becoming basic (Grey, 2008).

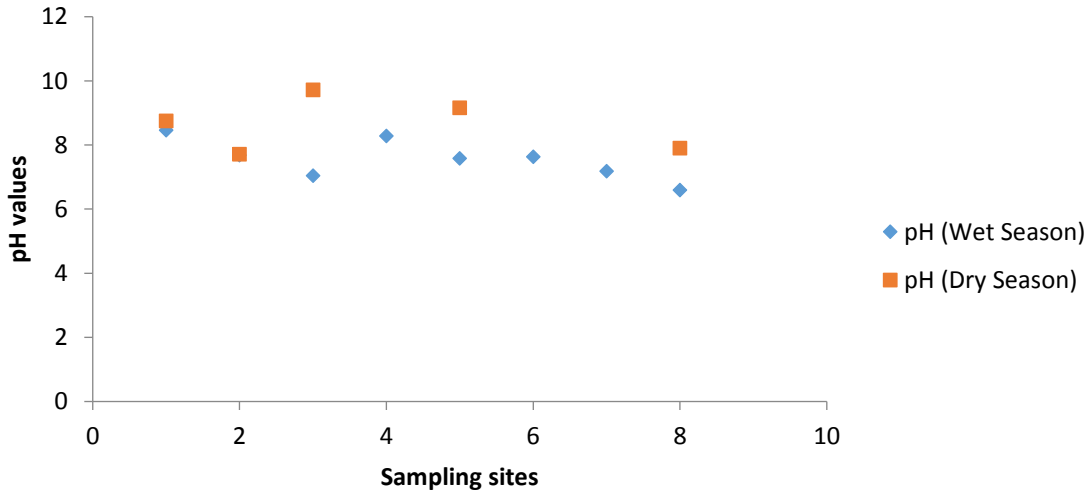

Figure 4.2 Variation of pH values at the different sampled sites during the wet and dry season

4.2.2 Implication of microorganisms

High amounts of *E.coli* and coliform bacteria colony-forming units per millilitre were observed in the dry season but there were zero units counted from similar inoculation during wet season sampling. Judging from the presence of domestic and wild animals at some water bodies, and the high values recorded in the dry season, the zero CFU/ mL results in the wet season may have been a result of a technical error rather than an actual depiction of the water's bacterial load. A possible error could be either with the handling or preparation of the petri films, inoculation, incubator, or samples. The results from the dry season show that the raw water, often used by residents during frequent pump breakdowns, most likely contains pathogens, as there is evidence of faecal contamination. Moreover, the inconsistent disinfection process means even the "treated" water is risky as well. This could not be proven experimentally during the dry season, since tap water was not available for sampling during the dry season visit. However, it is expected that its results would have been like those of site A, from which most tap water is abstracted and delivered to the tap system usually without disinfection (as outlined in section 1.4.5).

Likely sources of faecal contamination in Kamativi include both animals and humans. As noted during sampling, domestic and wild animals commonly drink from the reservoirs around the town. Under the current regime, the reticulated water supply in Kamativi is rationed due to the need to conserve power and enhance the longevity of pumps for the cash-strapped council. The supply is usually early in the morning and late in the afternoon for about an hour each time (S. Ndlovu, personal communication, April 21, 2016). Flush toilets, which form the majority of ablution facilities in Kamativi, require running water. In the absence of a constant water supply, some residents may be persuaded to defecate anywhere in the vast expanse of bush nearby. When it rains, faecal material may then be washed into rivers and dams.

4.2.3 Implications of other water quality parameters

Conductivity is a dependent factor, directly related to total dissolved solids (TDS) because it is the dissolved ions that allow the water to conduct electric current. As such, conductivity reflects the amount of dissolved substances and can be used as an approximation of TDS (APHA, 1995). This means that Kamativi water had values for conductivity (82 to 261 µS/cm) which reflected average TDS load of the water bodies with Site C's leading

concentrations attributable to high solute concentrations including elements like Li, major ions and an aggregation of other smaller concentrations of different ions.

The recommended turbidity limit for tap water, 5 FAU, was exceeded by the mean values obtained in Kamativi during both the wet and dry season sampling. Evidently the water treatment system's filtration mechanism is not efficient at reducing the turbidity to levels lower than 5 FAU. The control site H, which had inflows from feeder streams coming from the eastern side, had the highest recorded turbidity values for both seasons. Wild and domestic animals were observed at this site during sampling; their activities combined with the shallow depth of Site H, particularly in the dry season, likely contributing to the high turbidity.

The main impact of turbidity is aesthetic; however, it is important to eliminate high turbidity of water to effectively administer disinfection chemicals such as chlorine for treatment of drinking water (Grey, 2008). Turbidity, therefore, just like pH, makes the treatment of raw water more expensive and reduces the efficiency of disinfectants. Additionally, the suspended particles can result in adsorption of heavy metals or other toxic compounds such as organic pesticides (Grey, 2008).

Major ions are an important indicator of water quality. In almost all sites, the concentration of the ions showed significant variation between the wet and dry season, which is likely to reflect the influence of rain, seasonally related high evaporation, and rock weathering. The trend was generally for higher ion concentrations during the wet season, apart from sulphate and carbonate ions. Site C had high concentrations and did not conform to the trend in concentrations observed in other water bodies presented in Section 3.2.8. This could be likely due to its exposed boulders, loosened rock, and earth surfaces as well as quarry remains that could influence higher concentrations when water levels are lower in the dry season. Implications could include higher charge and hence solubility of oppositely charged elements, leading to higher trace elements concentration in such water (Grey 2008). This appears to be the case with Site C.

Correlation to arsenic

Some major ions were strongly correlated with elevated concentrations of toxic trace elements. Mg was positively correlated with both total and dissolved concentrations of As in a very strong manner in both the wet and dry seasons. Ca, Na and Mg had a strong correlation

with arsenic, which could form an important and simplified indicator for monitoring in future for tracking arsenic sources and taking note of increases in major ion species to flag possible spikes in arsenic.

4.2.4 Nutrients concentration in Kamativi

Nutrients are some of the well-monitored parameters in major catchment water bodies of Zimbabwe (Chinyama et al, 2015). Data from a 2009 report on water bodies in the same catchment show that the concentrations of NO_3-N and PO_4 in Kamativi were generally comparable to water bodies other than the Gwayi catchment average but lower than "Impacted Rivers and dams", that is, those close to dense human settlements, polluting farms, sewage plants or mines (Mweembe and Munkuli, 2009) (Table 4.2). The low nutrient values may be attributable to the absence of large scale agriculture in the Kamativi area. Large scale agriculture uses fertilisers that sometimes increase NO3-N levels in the water. The sewage plant in Kamativi is dysfunctional and is threatened by nitrate pollution; however, it is currently closed out from letting water flow into the environment but may actually be leaching nutrients into the ground water near it. Analysis of ground water may reveal results different from what was found in surface water during this research. This means the threat of nutrient pollution was not revealed by the study of surface water done here, but the sewage plant should be of concern to Kamativi authorities and measures should be taken to repair the dysfunctional sewage plant.

Table 4.2 Nutrient concentrations in some water bodies in the Gwayi catchment (Mweembe & Munkuli, 2009)

Kamativi	**Threat/ impact**	**NO_3-N**	**PO_4**
Kamativi	Tin mining	0.07mg/L–0.69 mg/L	0–0.45 mg/L
Gwayi River	Low threat from fishing	0.03–2.06 mg/L	< 0.77 mg/L
Mlibizi Dam	Farming and fishing	0.04–1.6mg/L	0.02–0.78 mg/L
Upper Umguza	Low sewage threat	0.024–5.8 mg/L	0.01–0.91 mg/L
Manzi-asiya dam	Multiple contamination	15.07–36.46 mg/L	0.01–1.86 mg/L

4.3 Particulate and dissolved trace elements

To further understand the composition of trace elements that were above stipulated ZW standards and WHO guidelines, particulate concentrations were calculated and a comparison

between dissolved and particulate concentrations was made to find the state of the trace elements concerned in the water. This can help responsible authorities when choosing a method of removal, where necessary.

4.3.1 Correlations between parameters

Consistent correlations between parameters help in understanding patterns in water parameters that may be used in monitoring and remediation, as well as establishing causative factors for the parameters of primary concern and others. Pearson correlation coefficient (PCC) (Table 4.3), reveal that most trace elements are strongly correlated to turbidity. This is likely due to trace elements on suspended sediment as well as fine colloidal matter. There's also a strong correlation between pH and DO which is characteristic of an effect of photosynthesis in aquatic and riparian plants (Chapman, 1996). Arsenic was strongly correlated to major cations and this could be tied to the practise of pumping out groundwater from underground mine shafts into surface water which was done during the mine's operational years (ZMDC, n.d.). Total arsenic concentrations had a strong correlation to the concentration of Li as well. Li, a component of some of the minerals in Kamativi (Table 1.2), had concentrations correlated to other trace elements including Pb, Al, Cu and Fe, thereby highlighting their links to the mine. These correlations are also relevant in the selection of methods for removal of trace elements, as discussed in Sections 4.7as part of recommendations for management.

Table 4.3 Correlations for water quality and trace elements concentrations in the wet and dry seasons.

	Al	As	Cu	Fe	Pb	Li	Mn	Zn	Na	K	Mg	Ca	pH	DO	Turb	
Al		-0.30	0.79	0.58	0.69	-0.56	0.95	0.82	-0.14	-0.02	-0.10	-0.65	-0.33	0.06	0.87	Al
As			0.28	-0.49	-0.42	0.83	-0.58	-0.33	0.93	0.80	0.90	0.89	0.49	0.37	0.45	As
Cu				0.67	0.69	-0.68	0.59	0.78	0.48	0.59	0.52	-0.07	0.19	0.51	0.81	Cu
Fe					0.69	-0.54	0.35	0.18	-0.32	-0.18	-0.28	-0.77	-0.36	0.03	0.87	Fe
Pb						-0.50	0.67	0.79	-0.29	-0.16	-0.25	-0.76	-0.44	-0.06	0.84	Pb
Li							-0.51	-0.55	-0.23	-0.47	-0.31	0.23	-0.41	-0.61	-0.88	Li
Mn								0.73	-0.42	-0.28	-0.38	-0.83	-0.42	-0.04	0.84	Mn
Zn									-0.17	-0.05	-0.13	-0.67	-0.33	0.07	0.88	Zn
Na										0.90	0.84	0.83	0.71	0.66	0.01	Na
K											0.82	0.70	0.78	0.77	0.22	K
Mg												0.79	0.73	0.69	0.08	Mg
Ca													0.69	0.46	-0.52	Ca
pH														0.92	0.08	pH
DO															0.43	DO
Turb																Turb
	Al	As	Cu	Fe	Pb	Li	Mn	Zn	Na	K	Mg	Ca	pH	DO	Turb	

Note. Strong linear dependences are shaded in yellow (±0.8 to ±0.89) and very strong ones in orange (±0.9 to ±0.99). Values of ±1 would be total linear relationships.

Arsenic – sources and correlations

Arsenic concentration was over the ZW standard limit in five out of six main water reservoirs in Kamativi (Sites A-F). Sources of arsenic vary: some is present as natural deposits in rock complexes and may be liberated as part of the mine's metallurgical effluent during processing; arsenic may also be released into the environment from pesticide residues and as a trace component of certain types of coal ash left behind after combustion. In some cases, arsenic may be naturally present at high concentrations in the groundwater (Bhattacharya et al., 2007).

In the case of Kamativi, there is a high likelihood of either some rock formations bearing arsenic, or a natural presence of arsenic in the groundwater, or both. This is because of the distribution pattern of arsenic between the sampled sites in comparison with the control sites. The arsenic concentration peaked at Site C (Figure 4.3. Arsenic concentrations had strong correlation with the major ions Li, Ca, K, Na and Mg. In site-by-site analysis, as shown in the previous chapter, the combined concentrations of arsenic are higher at Site A, Site C (quarry dam with exposed inner rock surfaces), Site D and Site F compared with Sites E, Site G and Site H. The common factor among the sites with high concentrations is their vicinity to the mining area, while those with lower concentrations are either upstream of the mine (controls Sites G and H) or do not receive any flow from the mine due to distance and topography (Site E) (Figure 4.3). Kamativi has a high water table, and reports indicate that during past operations ground water was regularly pumped out of the ground into surface reservoirs in order to keep mine shafts dry (ZMDC, n.d.). Therefore, if it is the case that groundwater may naturally have high arsenic concentrations, that property may have been transferred to surface water by this practice over the 54 years that the company operated.

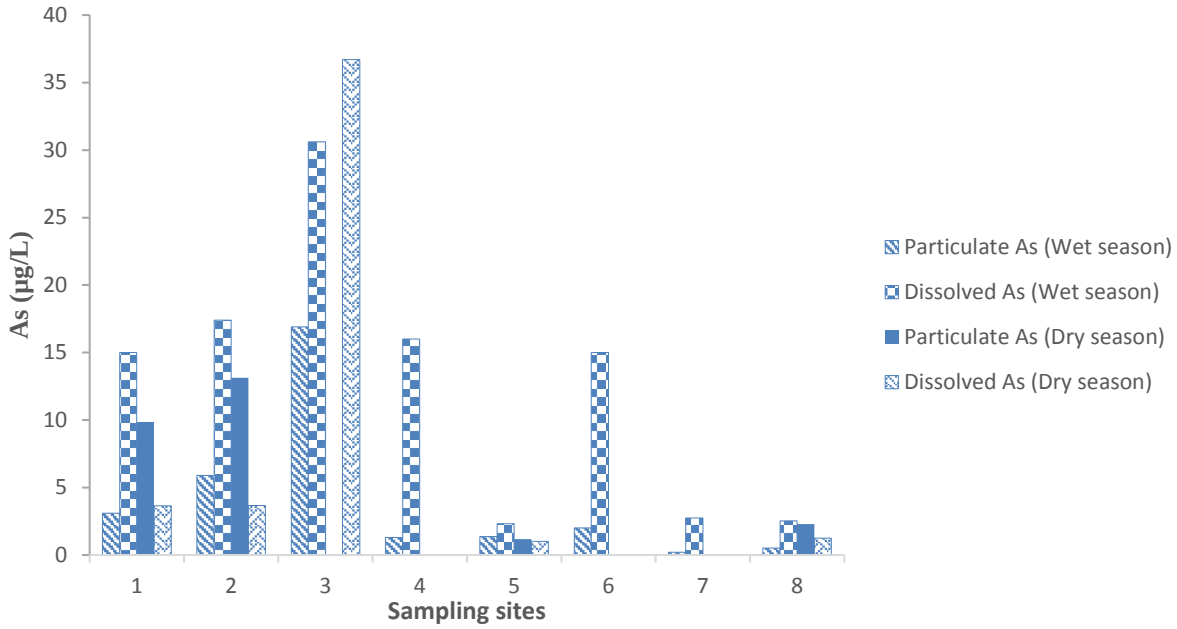

Figure 4.3 A comparison between concentrations of particulate and dissolved arsenic. Particulate concentrations were calculated from subtracting values for dissolved concentrations from total acid soluble concentrations.

Arsenic is highly toxic. Contaminated drinking water, food and irrigated crops are a significant threat to public health. Some of its long-term effects include certain types of cancer, skin lesions, developmental defects in children, heart-related diseases, neurotoxicity and diabetes (Tsai and Chou, 2003; Chen et al., 1995).

4.3.2 High lithium concentrations: causes and implications

Li concentrations were higher than any other trace element measured. Apart from the relative abundance of lithium-based minerals in Kamativi, such as zabuyelite (Li_2CO_3), amblygonite ($LiAl(PO_4)F$) and montebrasite [$LiAl(PO_4)(OH)$] (Thomson's Publications, 1984), its high instability and solubility likely contributes to its ubiquity in water, as evidenced by the consistently high dissolved Li concentrations as opposed to particulate compounds (Figure 4.4). Li had a strong correlation with As, Pb, and the major ions Ca and Mg (Table 4.3). Following a trend similar to As, Li concentration levels were a lot lower at Site E and at control Sites G and H (Figure 4.4). This is expected for an element associated with some of the minerals mined in the area. Site E lies about 6 to 8km to the north of the mine, which is also the northern end of the town, and has no flow from the mining grounds. This is a likely indicator of the influence of the mine on the concentration of trace elements in Kamativi's water. Similar trends are seen in the concentration of other trace elements.

Lithium is a nonessential element in humans without any known use, and neither is it readily assimilated during metabolism, before excretion. Lithium products are, however, used in medicine (Aggrawal, 2000). Li constitutes only about 7 mg of a healthy person's total mass. Studies, however, have shown that Li may be slightly toxic if taken orally, although the extent of toxicity and susceptibility varies with secondary toxins formed; individuals with 10 mg/L of Li_2CO_3 in blood can experience low toxicity and at 15 mg/L can experience impairment (Aggrawal, 2000). Lithium-based salts resulted in some deaths when LiCl was used as a dietary substitute for table salt (NaCl) in the 1940s (Hanlon et. al, 1949). Li, in sufficient concentrations may also cause internal blisters in the body due to it being an alkali metal.

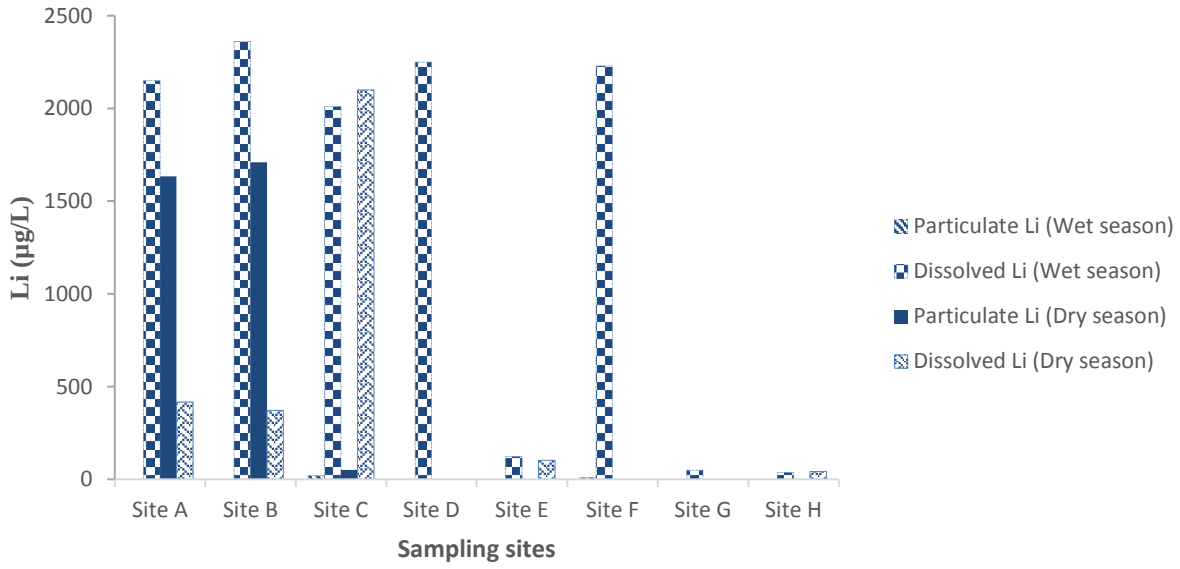

Figure 4.4 A comparison of dissolved Li to particulate Li. Particulate concentrations were calculated from subtracting values for dissolved concentrations from total acid soluble concentrations. Particulate Li is almost non-existent in the wet season due to the high solubility of Li compounds which make dissolved concentrations predominantly the main form of Li in aquatic bodies. Particulate amounts at Sites A and B are likely to be a result of stirred sediment taken up during sampling.

According to the Food and Agricultural Organization's (FAO) document on water quality for agriculture, plants readily take up Li from soil. Although it is not a dietary mineral, it may stimulate plant growth in small quantities; however, elevated concentrations are toxic to plants and can cause tissue damage, and therefore water which is high in Li may not be suitable for irrigation (FAO, 2016). Kamativi is not a commercial farming area but, from

observation, some residents practice small-scale horticulture and use surface water to irrigate their food plants, e.g., vegetables and fruit trees. Lithium in elevated concentrations is known to cause tissue injury to plants. The level of tolerance varies between plant types, with citrus known to have a lower tolerance than other plant type. The majority of plants will tolerate Li up to 5,000 µg/L while some citrus plants will begin to be negatively impacted by concentrations exceeding 75 µg/L (FAO, 2016). Closing off the mixing of water from open former mine pits and that from the town's drinking reservoirs could help reduce Li concentrations in the long run.

4.2.3 Implications of aluminium and manganese concentrations

Al and Mn were not a widespread problem but were above the WHO guideline limit on one occasion each. This means there is need to investigate further and monitor the concentrations over a long timeframe to establish whether a significant contamination threat exists. In the wet season, the total Al concentration was 273 µg/L at Site C, exceeding the WHO guideline limit of 200 µg/L. The total Al concentration at the control Site H had a concentration of 175 µg/L, which was below the guideline limit but higher than the concentrations in the other six sites. Mn concentrations for most sites were below the WHO limit, with the only exception being at the control Site H in the dry season where a particulate concentration of 978 µg/L compared with a dissolved concentration of 71.6 µg/L (Figure 4.6). Limitations in the number of replications for samples brought to NZ and those subsequently submitted for ICPMS analysis mean that reasons for the isolated peaks in concentrations of Al and Mn are not quite known. However, the two Li-based minerals amblygonite ($LiAl(PO_4)F$) and montebrasite, $[LiAl(PO_4)(OH)]$ are likely contributors of Al in Kamativi water (see section 1.4.3 and Table 1.2). Inadvertent stirring of sediment during sampling could have resulted in elevated concentrations as well, because particulate Al and Mn was particularly high (Figure 4.5 and Figure 4.6).

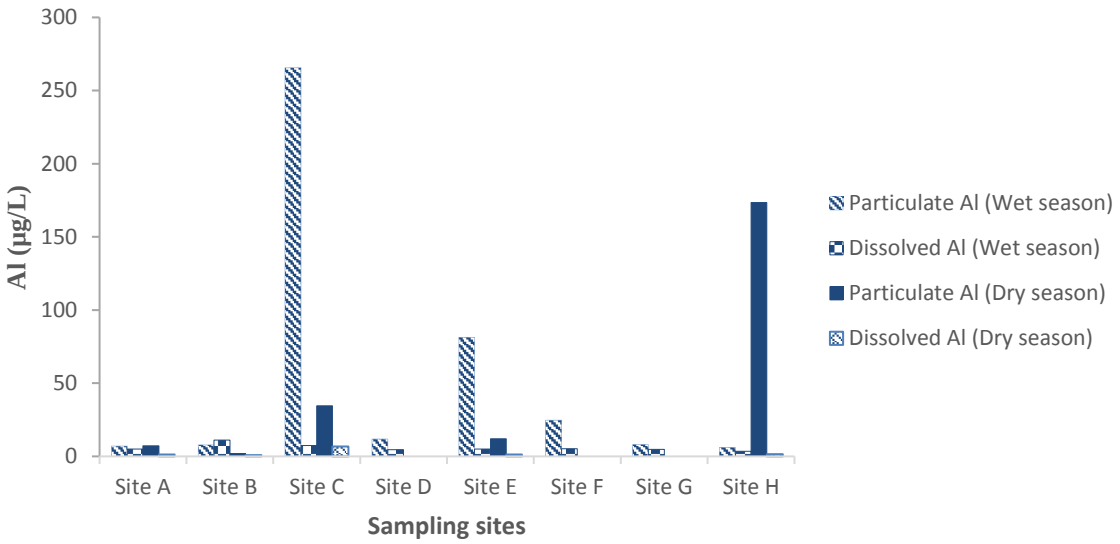

Figure 4.5 Comparison between particulate and dissolved Al concentrations. Particulate concentrations were calculated from subtracting values for dissolved concentrations from total acid soluble concentrations

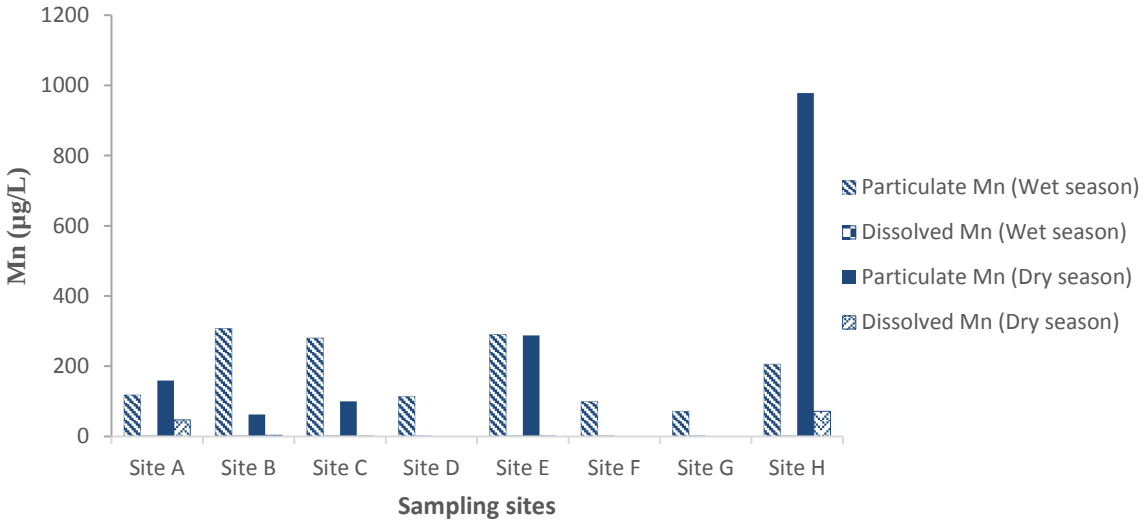

Figure 4.6 Comparison between particulate and dissolved Mn concentrations. Particulate concentrations were calculated from subtracting values for dissolved concentrations from total acid soluble concentrations

4.4 Low tin concentrations from ICPMS analysis

Tin is the main metal that was mined and processed in Kamativi. The unexpected consistently low concentrations of tin that were below detection limit (0.1µg/L), in Kamativi's surface water, may need analysis of further aspects of the environment such as sediments and soil to

get an empirically conclusive cause. The most probable reason for the low concentrations may be the relative stability and low dissolution properties of cassiterite (ITRI, 2012). The mining process in Kamativi involved a recovery phase for tin and this could have reduced the amounts of liberated Sn compounds washed off into the water (ZMDC, n.d.). Secondly, tin has not been mined in Kamativi for the past 23 years, since the closure of the mine. There is a high likelihood of most free detectable tin from the mining process having been relegated to soil and sediment (Howe and Watts, 2005). Sediment analysis was not part of the focus of this study. This could explain why tin was consistently below 0.1 µg/L.

4.5 Comparison of Kamativi water quality with other water bodies near mines.

A comparison was made with some water bodies impacted by mining in Zimbabwe. In 2012, the Zimbabwe Environmental Law Association (ZELA) investigated water quality complaints by villagers living near Marange diamond mine (ZELA, 2012). Another comparison was made with an abandoned gold mine in Beatrice which has several water pools as part of the abandoned minefields (Ravengai et al, 2005). Some of the most polluted sites of these sites were compared with Kamativi Site C (a former mine quarry site) and the results presented in Table 4.4. From these examples, Joyce mine slime dam had much higher arsenic concentration compared with Kamativi Site C, while the Save River tributary near Marange Diamond mine had no detectible arsenic concentrations. This means Kamativi is among the polluted waters of current and former mining sites, although it is not the worst, even in terms of arsenic pollution. Gold mines in Zimbabwe have been notorious for environmental pollution, because of panning and other informal activities that may happen in the peripheries of gold deposit areas (Akcil and Koldas, 2006).

However, a distinction must be made regarding the role of the other impacted water bodies presented in Table 4.4. While parts of the Save River are used by villagers as a drinking water source, areas around the Joyce mine do not serve such purpose due to fears of other pollutants used in gold mining such as cyanide, mercury, etc. Arsenic, though, is not a heavy metal commonly tested for in routine water analysis studies (Smedley and Kinniburgh, 2002). Therefore, data on arsenic is scanty in Zimbabwean cities' water quality analysis data where monitoring is routine and consistent.

Table 4.4 Comparison of Kamativi's water to other waterbodies that are in close proximity to a mine in Zimbabwe (Chinyama et al, 2015; Meck, et al, 2006; Ravengai et al, 2005; Zimbabwe Environmental Law association, 2012)

Type of mine	Water body	Catch-ment	*E. coli* (CFU/ mL)	Coliforms (CFU/ mL)	As (µg/L)	Fe (µg/L)	Al (µg/L)	Mn (µg/L)
Diamond mine	Save River tributary (Site 8)	Save	>10	1	n/a	77850	0.28	0.42
Tin mine	Kamativi Site C	Gwayi catch-ment	>10	2	47.50	781	273	281
Gold mine	Joyce mine slime dam	Sanyati	n.d.	n.d.	175	32	34.56	not tested

4.6 Key summary points on Kamativi water

- The pH of Kamativi water indicates a warning of potentially abnormal water quality, even though the pH by itself is not a primary concern.
- Microbiological results indicate the likelihood of pathogens in Kamativi water.
- High turbidity in tap water is evidence of the inefficiency of the filtration and sedimentation process carried out as part of domestic water treatment in Kamativi, and may indicate worsening disinfection and promoting of trace element adsorption to suspended particles in the water.
- Arsenic concentration is above the stipulated ZW standards in Kamativi water bodies, and potentially for other trace elements like Al, Mn, etc.
- The risk posed by trace element pollution appears more pronounced in the sites downstream and closer to the mining grounds. Indications are that the mine has a polluting influence on local water.

4.7 Recommendations for management

Resuts obtained from this study demonstrate a need for corrective action for Kamativi's water.

4.7.1 Monitoring

The first and most important recommendation is for the establishment of a permanent monitoring system for Kamativi. This should be drafted as part of standard operating procedures that are to be followed as a mandatory requirement. It is recommended that key indicators of water quality be measured at a regular frequency, e.g., daily or weekly depending on resources, and the data obtained be used to inform management and treatment of the water. It is also imperative that training be given to employees who will be carrying out monitoring, to ensure that results are reliable. Monitoring will also help to evaluate whether any corrective action is being effective over time. It will be a main means of assessing progress for the corrective action taken in treatment of the water.

4.7.2 Overhaul and upgrade of water treatment system

The results of water quality assessment show that the water treatment system at Kamativi is largely dysfunctional and needs an urgent overhaul.

Microbiological quality improvement will require adequate and consistent practice of the disinfection process, which is often omitted, as mentioned in Chapter 1 (Figure 1.9b). There is a need for the standardised and documented procedures to be adhered to, e.g., correct amounts of coagulant ($AlSO_4$) to be added every time to ensure sufficient flocculation of suspended solids, and removal of the resultant flocculants from the water before it is released. Replenishment of the sandbed filters and an allowance of ample time for sedimentation to take place should be done to help the process of reducing turbidity and enhancing the efficiency of the next stage of disinfection. This may also lower the costs required for the disinfection process, as fewer chemicals will be needed for less turbid water. Procurement of disinfection chemicals should a top priority.

4.7.3 Remediation for arsenic and other trace elements

The cheapest way to deal with polluted resevoirs may be to avoid them altogether, if feasible. Results of arsenic concentration showed that Site E and the control sites had much lower concentrations, which complied with standard guidelines. According to a senior water procurement worker at Kamativi, Mr Phiri (personal communication April 21, 2016), there

are existing back-up pipes that can bring water to the mine from Site E and also from Gwayi River (not sampled but close to Site G), both of which can be alternative sources for drinking water, with less pollution. The main water reservoirs, Site A and Site B, would require substantive treatment for arsenic to make the water safe for consumption.

Treatment options

Arsenic in water has two main forms: As (V) mostly in aerobic water such as surface water or ground water close to the surface, and As (III) found mostly in anaerobic water such as in ground water. This difference is mainly due to higher dissolved oxygen in surface water compared with the relatively anaerobic conditions in ground water (Oregon Health Authority – OHA, 2016). Arsenite (H_3AsO_3) and arsenate ($H_2AsO_4^-$) are the naturally occurring oxyanions of As (III) and As (V) in that order, and they carry a neutral and negative charge respectively in most waters (Smedley and Kinniburgh, 2002). Other compounds of As (III) and As (V) exist which have different charges.

Sampled water bodies in Kamativi were all surface sources with DO values ranging from 6.51 mg/L to 13.02 mg/L, hence we expect a prevalence of As (V) (Smedley and Kinniburgh, 2002). However, methods of removal for both species will be discussed since underground water is also used by some people in Kamativi, even though it was not covered under the scope of this research. The negative charge on arsenate makes it easier to remove from water by exploiting its charge (Table 4.6). Oxidation of arsenite to arsenate prior to treatment can improve the efficiency of its removal (OHA, 2016).

Fe concentrations in the water are important in that where there is high Fe concentration (> 300µg/L) and a strong correlation between As and Fe, then Fe-removal technologies can be used to reduce As. Where Fe concentrations are below 300 µg/L, adsorptive media such as reverse osmosis (RO) and ion exchange units are best suited for treatment (USEPA, 2014). Odour, colour, taste and system-fouling problems may result if these latter methods are used on water with high Fe levels (USEPA, 2014). However, ICPMS results from Kamativi had dissolved Fe concentrations ranging from 0.96 µg/L to 19.2 µg/L, while total HNO_3 soluble concentrations ranged from 38.1 µg/L to 813 µg/L, with values over 300 µg/L at site C, site E and site H (Figure 3.18). Site C is a former mine quarry site and is the only one with high values of both Fe and As concentrations. Site E and Site H have low As concentrations. The main Kamativi reservoirs, Site A and Site B, happen to have low Fe concentrations and would therefore be suited for the second option. Tables 4.5 to 4.7 present summaries of some

common treatment methods that can be applied at both household and public levels for the Kamativi situation. Section 4.7.4 discusses other recommendations that were not covered by the scope of this research but may be more practical in the short term in the face of funding constraints.

Table 4.5 Reverse osmosis (RO) as a method of arsenic removal from water

Descriptor	**Advantages**	**Disadvantages**
Reverse osmosis - filtration at a molecular level by forcing water through a special, selective membrane with microscopic pores that are specially sized to allow water molecules through, while trapping larger inorganicslike As, Pb and Fe. It consists of a pre-filter for sand and grit, a commercially produced membrane where RO occurs, and an activated carbon filter for taste and odour control. The treated water is relayed to a storage tank.	It is very effective at removing inorganic constituents (95%). Requires little maintenance and no additional chemicals. Smaller units can be privately acquired and installed in homes or at any drinking point to produce up to about 11 litres a day.	Smaller units produce little water while large systems are much more expensive. If installed at a household pipe point of entry, RO can cause corrosion control problems in plumbing, which can elevate concentrations of Pb and Cu. If As (III) is prevalent, pre-oxidation is necessary which complicates the process and increases costs Treated water may taste bland because the inorganic minerals are removed If high Fe or Mn levels are present, additional pretreatment will be required to remove them.

(USEPA, 2014; OHA, 2016; Faust, 1998)

Table 4.6 Anion exchange resins as a means of removal of arsenic from water

Descriptor	**Advantages**	**Disadvantages**
Anionic exchange systems use physico-chemical ion exchange process to exchange ions between a resin bed and the source water flowing through. The net effect is softening the water by removal of Fe, Mn and reduction of As and NO_3 concentrations. Specific contaminant removal is determined by the composition of the resin bed used.	Anionic exchange requires little maintenance; additional salt is added every few weeks. It can be installed to treat at household level with higher output than RO.	Other constituents in water can compete with As for the resin sites, thereby reducing the effectiveness, especially for highly turbid waters such as in Kamativi. Very low pH can occur in treated water due to anion removal and high levels of chloride, which can cause corrosion of pipes thereby elevating Cu and Pb levels In the event of failure, all As held by the resin at that time can be released at one go, resulting in a surge in As concentration in the treated water.

(USEPA, 2014; OHA, 2016; Faust, 1998)

Table 4.7 Iron oxide filter systems as a method of arsenic removal from water

Method Descriptor	**Advantages**	**Disadvantages**
Iron oxide filter systems have granular filters with large amounts of surface area and an affinity for arsenic to adhere to its surface. It works by adding ferric chloride ($FeCl_3$), to water to create $Fe(OH)_3$ (Iron hydroxide) and $HCl_{(aq)}$ (also lowers pH). $3H_2O + FeCl_3 \rightarrow Fe(OH)_3 + 3HCl$ $Fe(OH)_3$ is a strong adsorbent of As at low pH. The Cl^- oxidises Fe from Fe^{2+} to Fe^{3+}, which bonds with OH^-, thereby forming more adsorbent. Arsenic adsorbs onto $Fe(OH)_3$ creating larger complexes that are then filtered off the water.	Effective for both As (III) and As (V) treatment. Can be used at both public and household level They remove other inorganic constituents. Simple installation and operation. Can be disposed as nonhazardous waste since no free As is released.	Adsorptive media needs regular replacement. Elevated concentrations of Fe, Mn, SO_4 and SiO_2 can reduce effectiveness.

(USEPA, 2014; OHA, 2016; Faust, 1998)

4.7.4 Other recommendations

Funding for a well-maintained water treatment system for a small town with no industrial backing, such as Kamativi, is likely to remain a challenge unless the mining operations are resumed or another economic activity is promoted to empower residents to pay bills that the responsible council levies for water service provision. While reports continue to be announced on the imminent reopening of the Kamativi mine (Kazunga, 2017), the council can, in the meantime, seek assistance from the government-funded parastatal Zimbabwe National Water Authority (ZINWA) to help in managing the unhealthy water situation. They should also prioritise educating residents on the dangers of highly polluted water sources such as Site C (former quarry dam). The new mining prospector will have to prioritise not only managing the existing pollution situation, but prevent any further worsening of the town's water reservoirs when and if operations are revived.

5.0 Conclusions

Suitability for consumption

The drinking water in Kamativi does not meet the standards for Zimbabwean drinking water; it is therefore not suitable for consumption in its current state, and it presents a health risk to residents. Treatment of drinking water is needed to address the following concerns:

- Microbiological results indicate the likelihood of pathogens in Kamativi's raw water. The tested water contained *E. coli* and coliform bacteria (in the dry season), which are indicator of faecal contamination. This, when considered with the fact that disinfection is not always undertaken for tap water, presents a contamination risk.
- High turbidity in tap water is evidence of the inefficiency of the filtration and sedimentation process carried out as part of domestic water treatment in Kamativi, and perhaps indicating a poorer disinfection process, and causing trace element adsorption to suspended particles in the water.
- Concentrations of arsenic were high and exceeded the drinking water standard limit. This presents health risks that are discussed in Section 3.4.1.
- Aluminium and manganese concentrations exceeded WHO guidelines in some water bodies (i.e., Site C and Site H)
- In general, the controls had lower concentrations of trace metals than the water bodies closer to the mine in 8 out of 10 trace elements that were analysed for a full quantitative ICP-MS scan (Tables 3.5–3.8). The main water reservoirs being used for the public drinking water system are very close to the mine and as such are exposed to pollution from the mine, especially now that there is no evidence of sufficient preventive measures in place.

Environment

- The water from the main Kamativi dam (Sites A and B), the quarry dam (Site C) and all streams and rivers running through the town, may not be suitable for crop irrigation due to the risk of toxic levels of trace elements, particularly arsenic, that could be taken up by

plants and pose a risk to consumers. High lithium levels in most water bodies in Kamativi have a potentially damaging effect on citrus plants.

- There is evidence of mine-related pollution in the water in Kamativi. Water bodies downstream and close to the mine generally have higher concentrations of pollutants.

Summary of implications for water management in Kamativi

- There is an urgent need to improve service delivery and shorten rationing times, to discourage residents from using the open bush for defecation where applicable. Pit latrines can be built in all public places and closer to residential areas for use when there is an interruption in the reticulated water supply. These can be managed and maintained at community or household level.
- Renewal and maintenance of a fully functional water treatment system is needed. This will ensure that disinfection, among other stages illustrated in Figure 1.9 (a), are carried out consistently and efficiently
- Technical corrective action needs to be taken to avert the health impact of trace metals in high concentrations. There is a need to adopt techniques to treat for trace metals, particularly arsenic. Some of the most common options are discussed in section 4.5.3. This will also entail training of personnel to introduce new techniques and equipment
- It may be necessary to seek government funding in the short term as a matter of urgency, and it is also recommended that any prospective mining company that plans to reopen the mine take measures to reduce existing pollution levels and prevent further pollution from renewed operations.
- Monitoring and evaluation needs to be adopted as a standard operating procedure for the water management sector at Kamativi.

5.1 Limitations

The study was subject to limitations in the time allocated for sampling and funding to assess a wider scope. The 2015–2016 rainy season in Southern Africa in general was characterised by an El Nino-induced drought, which meant that the rainy season in Kamativi was not a typical one. There was less rain than usual and rivers dried out sooner than normal (Zimbabwe Meteorological Services Department, 2015).

The colorimeter was held up at the airport during the first trip after a misunderstanding with customs, which prevented field measurements for NO_3-N and PO_4 at the time. These were only assessed four weeks later back in New Zealand, which was not ideal since the samples had travelled over a long distance and time without being frozen which presented a large possibility of nutrient loss through organism activity in the samples.

The two control sites were chosen exclusively for their geographical location, i.e., upstream of the mining area water flows. These sites were imperfect for other parameters that may be affected by other factors other than the Kamativi mine. The results of experiments on physico-chemical parameters and some trace elements may not reflect a clear distinction pattern for the effect of wild animals and other outside variables that were not covered by this research.

4.6 Recommendations for future research

To further understand the impact of Kamativi tin mine on the water in Kamativi, it is imperative to evaluate whether the impact is historic or ongoing. It is of great importance to those managing the water supply system to understand this. In the event of the mine resuming operations, the environmental impact assessment should also involve predictive analysis on issues to do with heavy metal pollution and acid mine drainage. A proper closure plan should be required from prospectors taking into account results from such a predictive analysis. I would also recommend evaluation of ground water in boreholes around Kamativi as this was not covered by this research due to resource and time constraints. This would be particularly important for evaluating arsenic and other trace elements that may be naturally available in ground water in elevated concentrations. The geology of the mining area will also need to be studied further to ascertain the origin and speciation of known heavy metals that are associated with the mine.

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APPENDICES

Appendix 1: Raw data from water quality sampling in the wet season

	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.26	7.71	8.29	7.78	7.14	7.63	7.18	6.8
DO (mg/L)	11.8	7.49	6.31	12.04	8.05	9.8	10.84	6.59
Temp (°C)	25.5	25.7	26.2	26	25.7	20.3	25.6	26.2
Conductivity (mS/cm)	200.7	215.5	257	112.2	120.3	240.6	98.4	83.2
Turbidity (FAU)	29	21	32	38	47	16	46	98
Ecoli (CFU/ml)	0	0	0	0	0	0	0	0
Coliforms (CFU/ml)	0	0	0	0	0	0	0	0
NO_3-N (mg/L)	0.4	0.2	0.2	0.1	0.2	0.1	0.3	0.7
PO_4 (mg/L)	0.21	0.12	0.45	0.12	0.22	<DL	0.41	0.42
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.65	8.33	8.23	7.89	7.66	7.97	7.07	6.7
DO (mg/L)	12.05	7.68	7.04	11.9	8.61	9.05	12.08	6.5
Temp (°C)	26.3	26.1	26.4	26.3	26.9	21.1	26.2	26.4
Conductivity (mS/cm)	202.3	216.7	263.6	112.5	112.1	200.8	97.9	79.4
Turbidity (FAU)	26	20	32	34	39	13	37	95
Ecoli (CFU/ml)	0	0	0	0	0	0	0	0
Coliforms (CFU/ml)	0	0	0	0	0	0	0	0
NO_3-N (mg/L)	0.4	0.2	0.2	0.1	0.2	0.1	<DL	0.7
PO_4 (mg/L)	0.21	0.12	0.45	<DL	0.22	0.1	<DL	0.42
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.46	8.24	8.41	8.28	7.58	7.42	7.78	6.9
DO (mg/L)	11.57	7.72	6.92	11.42	8.6	9.63	12.35	6.45
Temp (°C)	26.5	26.3	26.3	26.1	27.1	20.8	26.9	26.6
Conductivity (mS/cm)	202.6	217.4	260.8	113.8	118.9	208.2	98.5	83.4
Turbidity (FAU)	24	24	35	39	42	10	41	93
Ecoli (CFU/ml)	0	0	0	0	0	0	0	0
Coliforms (CFU/ml)	0	0	0	0	0	0	0	0
NO_3-N (mg/L)	<DL	<DL	0.1	0.1	<DL	<DL	0.1	0.1
PO_4 (mg/L)	0.11	<DL	<DL	<DL	<DL	<DL	<DL	0.42

Appendix 2: Raw data from water quality sampling in the dry season

	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.79	7.77	9.75	-	9.16	-	-	7.9
DO (mg/L)	9.95	7	13.7	-	11.02	-	-	8.33
Temp (°C)	21.7	23.6	24.9	-	24.7	-	-	21
Conductivity (mS/cm)	241.5	253.4	261.3	-	142.4	-	-	149.5
Turbidity (FAU)	25	13	58	-	67	-	-	91
NO_3-N (mg/L)	0.3	0.1	0.2	-	0.2	-	-	0.9
PO_4 (mg/L)	0.2	0.15	0.44	-	0.25	-	-	0.38
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.74	7.76	9.7	-	9.12	-	-	7.86
DO (mg/L)	9.84	6.89	12.99	-	10.56	-	-	8.15
Temp (°C)	22.2	23.9	20	-	25.4	-	-	25.2
Conductivity (mS/cm)	237.4	250.1	257.2	-	145	-	-	150.3
Turbidity (FAU)	21	10	52	-	50	-	-	96
Ecoli (CFU/ml)	105	0	109	-	169	-	-	305
Coliforms (CFU/ml)	0	0	0	-	0	-	-	2
NO_3-N (mg/L)	0.4	0.2	0.2	-	0.2	-	-	0.6
PO_4 (mg/L)	0.15	0.17	0.39	-	0.3	-	-	0.4
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.86	7.71	9.72	-	9.22	-	-	7.89
DO (mg/L)	9.93	7.76	13.34	-	10.94	-	-	8.52
Temp (°C)	15.4	17.4	18.6	-	19.3	-	-	16.2
Conductivity (mS/cm)	238.1	249.6	262.4	-	145.5	-	-	148.7
Turbidity (FAU)	27	15	53	-	56	-	-	90
NO_3-N (mg/L)	0.5	0.3	0.3	-	0.2	-	-	0.5
PO_4 (mg/L)	0.27	0.09	0.55	-	0.16	-	-	0.54

Appendix 2 (continued…)

	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.75	7.7	9.8	-	9.18	-	-	7.87
DO (mg/L)	10.38	7.78	13.97	-	10.9	-	-	8.93
Temp (°C)	16.3	13.7	13.9	-	14.6	-	-	15.4
Conductivity (mS/cm)	233.7	250.9	262.1	-	139.6	-	-	147.8
Turbidity (FAU)	25	14	54	-	51	-	-	89
NO_3-N (mg/L)	0.4	0.2	0.2	-	0.2	-	-	0.7
PO_4 (mg/L)	0.22	0.07	0.42	-	0.17	-	-	0.36
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.39	8.04	9.04	-	9	-	-	7.99
DO (mg/L)	11.79	6.93	12.36	-	11.4	-	-	11.42
Temp (°C)	14.32	17.65	16.49	-	19.66	-	-	18.25
Conductivity (mS/cm)	249.7	259.2	275	-	153.6	-	-	109.5
Turbidity (FAU)	27	11	52	-	56	-	-	94
Ecoli (CFU/ml)	95	3	96	-	104	-	-	>100
Coliforms (CFU/ml)	0	1	3	-	6	-	-	13
NO_3-N (mg/L)	0.4	0.3	0.2	-	0.1	-	-	0.5
PO_4 (mg/L)	0.2	0.06	0.42	-	0.3	-	-	0.53
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.01	7.89	8.99	-	8.89	-	-	7.69
DO (mg/L)	10.38	6.99	12.46	-	11.45	-	-	11.18
Temp (°C)	14.25	17.71	17.96	-	20.01	-	-	19
Conductivity (mS/cm)	237.1	247.4	264.7	-	142	-	-	112.4
Turbidity (FAU)	27	9	48	-	49	-	-	91
NO_3-N (mg/L)	0.3	0.1	0.2	-	0.1	-	-	0.7
PO_4 (mg/L)	0.18	0.08	0.34	-	0.15	-	-	0.34
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.22	7.63	9.01	-	8.96	-	-	7.77
DO (mg/L)	11.34	6.89	12.75	-	11.36	-	-	11.42
Temp (°C)	14.24	17.15	17.74	-	19.89	-	-	20.49
Conductivity (mS/cm)	232.3	269.7	258.7	-	150.9	-	-	115.6
Turbidity (FAU)	22	11	58	-	57	-	-	86
NO_3-N (mg/L)	0.3	0.1	0.3	-	0.4	-	-	0.8
PO_4 (mg/L)	0.17	0.15	0.47	-	0.25	-	-	0.44
	site A (D1)	site B (D2)	site C (QRY)	site D (SS)	site E (No. 4)	site F (HTP)	site G (KMB)	site H (20)
pH	8.42	8.04	8.89	-	9.14	-	-	7.67
DO (mg/L)	11.37	7.13	12.59	-	11.97	-	-	11.71
Temp (°C)	20.16	23.59	24.11	-	25.83	-	-	24.37
Conductivity (mS/cm)	240.1	237.7	247.3	-	149.4	-	-	108.5
Turbidity (FAU)	20	9	53	-	50	-	-	94
NO_3-N (mg/L)	0.6	0.3	0.1	-	0.2	-	-	0.8
PO_4 (mg/L)	0.29	0.19	0.57	-	0.18	-	-	0.37

Appendix 3: Quantitative raw data for total HNO_3 acid soluble trace elements in the wet season

	A	B	Bdup	C	D	E	F	G	H	BLANK
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Li	2110	2280	2300	2030	2030	114	2240	47.2	25.8	14.1
B	14	16.8	17.3	43	15.1	12.3	14.4	6.02	4.97	4.37
Na	19100	20800	20700	25700	18600	4070	20200	1920	1580	171
Mg	4760	4710	4730	10900	4550	3480	4940	2840	2480	78.1
Al	12	19	21.1	273	16.3	86.4	30	12.8	9.51	3.87
K	8980	10100	9800	9490	8470	9820	8750	5210	4360	147
Ca	12400	12700	12500	11000	12000	10800	12800	10100	9560	187
Ti	0.341	0.31	0.518	5.03	0.399	1.13	0.441	0.285	0.254	0.0988
V	0.694	0.61	0.602	6.16	0.667	1.12	1.13	0.265	0.359	<DL
Cr	0.161	0.163	0.151	0.436	0.122	0.199	0.159	0.108	0.0968	0.0952
Mn	119	309	306	281	114	291	99.6	72.6	206	3.23
Fe	207	213	212	781	199	444	166	101	163	4.54
Co	0.258	0.379	0.362	0.739	0.223	0.731	0.245	0.253	0.326	0.00795
Ni	0.583	0.549	0.524	1.7	0.584	1.01	0.448	0.567	0.712	0.0569
Cu	3.81	1.51	1.26	4.49	2.06	1.61	2.2	1.7	0.963	0.19
Zn	3.49	13.7	13.6	5.84	5.06	4.71	15.9	6.56	6.17	0.776
As	18.1	23.3	23.1	47.5	17.3	3.67	17	2.95	3.05	0.214
Zr	0.0502	0.0519	0.0424	0.425	0.0276	0.0702	0.0393	0.019	0.00691	0.00132
Nb	0.0729	0.0624	0.0519	0.079	0.0368	0.0323	0.0303	0.0244	0.0181	0.0156
Mo	1.43	1.44	1.4	2.5	1.34	0.292	1.49	0.173	0.0692	0.0262
Cd	0.0399	0.0353	0.0268	0.0688	0.0182	0.02	0.0166	0.00713	0.00528	0.403
Sb	0.11	0.0964	0.0933	0.206	0.069	0.0468	0.0807	0.0635	0.0502	0.00821
Ta	0.212	0.193	0.183	0.257	0.164	0.148	0.154	0.131	0.121	0.117
W	31.1	125	123	2.68	68.3	1.72	1	0.574	0.388	0.239
Pb	0.274	0.324	0.327	2.66	0.27	1.04	0.662	0.252	0.229	0.0245

Appendix 4: Quantitative raw data for dissolved trace elements in the wet season

	A	B	C	D	E	F	G	H
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Li	2150	2360	2010	2250	124	2230	49.2	36.4
B	15.1	17.5	44.7	14.8	14.4	16.3	7.24	6.14
Na	19100	20700	25500	19500	4400	19700	2010	2040
Mg	4600	4830	9950	4600	3750	4820	2960	2870
Al	5.04	11.2	7.42	4.55	4.95	5.3	4.68	3.5
K	8060	8450	8570	8080	10900	8590	5380	5340
Ca	12100	12900	9860	12100	10200	12600	10400	10100
Ti	0.924	2.02	0.53	0.3	0.253	0.212	0.252	0.13
V	1.59	0.914	2.47	0.557	0.498	0.943	0.197	0.154
Cr	0.821	0.633	0.441	0.276	0.276	0.189	0.153	0.109
Mn	0.831	0.734	0.532	0.209	0.326	0.56	0.648	0.344
Fe	3.09	19.2	2.82	1.48	4.71	3.94	3.63	2.02
Co	0.82	0.567	0.483	0.252	0.252	0.227	0.179	0.147
Ni	1.06	0.808	1.28	0.433	0.79	0.427	0.628	0.925
Cu	1.76	3.74	1.9	3.12	1.29	1.59	1.24	2.67
Zn	7.96	10.7	8.06	9.18	1.34	6.54	4.11	5.13
As	15	17.4	30.6	16	2.31	15	2.74	2.53
Zr	0.939	0.597	0.612	0.23	0.162	0.112	0.0734	0.0513
Nb	0.938	0.686	0.544	0.29	0.223	0.16	0.123	0.0833
Mo	2.28	2.05	3.16	1.59	0.519	1.74	0.262	0.195
Cd	0.744	0.556	0.342	0.215	0.155	0.103	0.0774	0.0494
Sb	0.81	0.622	0.546	0.27	0.224	0.162	0.14	0.134
Ta	0.968	0.761	0.76	0.443	0.353	0.308	0.256	0.22
W	0.865	0.707	0.789	0.373	0.134	0.196	0.0552	0.0224
Pb	0.666	0.548	0.345	0.23	0.244	0.105	0.085	0.0476

Appendix 5: Raw data from the semi quantitative scan in the wet season.

Only the semi-quantitative data for which 10 ug/L (ppb) standard was reading correctly have been reported

	Li		V		Cr		Mn	
Sample Name	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit
0	<229.92	ng/l	66.85	ng/l	141.12	ng/l	121.92	ng/l
10ppb	9.95	ug/l	9.93	ug/l	9.86	ug/l	9.88	ug/l
Site A	2.08	mg/l	807.39	ng/l	120.34	ng/l	160.68	ng/l
Site B	2.31	mg/l	347.30	ng/l	98.61	ng/l	247.13	ng/l
Site C	1.91	mg/l	2.04	ug/l	86.19	ng/l	199.63	ng/l
Site D	2.26	mg/l	333.74	ng/l	74.67	ng/l	26.28	ng/l
Site E	117.15	ug/l	313.96	ng/l	101.27	ng/l	163.34	ng/l
Site F	2.26	mg/l	791.21	ng/l	56.05	ng/l	455.31	ng/l
Site G	42.42	ug/l	94.88	ng/l	43.64	ng/l	568.53	ng/l
Site H	36.51	ug/l	74.07	ng/l	16.16	ng/l	279.13	ng/l
Site A, total acid soluble (aa)	2.02	mg/l	569.68	ng/l	74.67	ng/l	118.03	ug/l
Site B (aa)	2.35	mg/l	546.24	ng/l	99.05	ng/l	320.98	ug/l
Site C (aa)	1.91	mg/l	5.89	ug/l	356.78	ng/l	283.41	ug/l
Site D (aa)	2.05	mg/l	586.37	ng/l	64.03	ng/l	120.59	ug/l
Site E (aa)	108.14	ug/l	1.07	ug/l	150.93	ng/l	305.61	ug/l
Site F (aa)	2.18	mg/l	991.52	ng/l	128.76	ng/l	100.42	ug/l
Site G (aa)	45.51	ug/l	204.14	ng/l	64.91	ng/l	77.16	ug/l
Site H (aa)	25.40	ug/l	300.95	ng/l	46.30	ng/l	218.20	ug/l
blank	12.30	ug/l	-48.65	ng/l	35.66	ng/l	2.81	ug/l

	Co		Ni		Cu		Zn	
Sample Name	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit
0	44.40	ng/l	159.65	ng/l	97.61	ng/l	330.53	ng/l
10ppb	9.96	ug/l	9.84	ug/l	9.90	ug/l	9.67	ug/l
Site A	151.33	ng/l	317.96	ng/l	1.10	ug/l	7.01	ug/l
Site B	90.34	ng/l	249.52	ng/l	3.28	ug/l	9.96	ug/l
Site C	152.89	ng/l	785.91	ng/l	1.53	ug/l	7.78	ug/l
Site D	53.44	ng/l	188.56	ng/l	3.01	ug/l	9.29	ug/l
Site E	82.20	ng/l	524.49	ng/l	1.11	ug/l	1.02	ug/l
Site F	106.28	ng/l	271.90	ng/l	1.53	ug/l	6.54	ug/l
Site G	95.33	ng/l	477.19	ng/l	1.19	ug/l	3.79	ug/l
Site H	86.58	ng/l	769.71	ng/l	2.61	ug/l	5.17	ug/l
Site A, total acid soluble (aa)	188.24	ng/l	423.69	ng/l	36.45	ug/l	3.11	ug/l
Site B (aa)	346.32	ng/l	432.38	ng/l	1.37	ug/l	14.24	ug/l
Site C (aa)	730.72	ng/l	1.52	ug/l	4.50	ug/l	5.86	ug/l
Site D (aa)	189.18	ng/l	507.08	ng/l	2.04	ug/l	5.13	ug/l
Site E (aa)	737.00	ng/l	902.95	ng/l	1.63	ug/l	4.59	ug/l
Site F (aa)	192.93	ng/l	326.65	ng/l	2.13	ug/l	15.65	ug/l
Site G (aa)	239.57	ng/l	483.42	ng/l	1.38	ug/l	7.08	ug/l
Site H (aa)	316.26	ng/l	663.89	ng/l	903.99	ng/l	6.62	ug/l
blank	-36.90	ng/l	-47.74	ng/l	152.20	ng/l	546.99	ng/l

Appendix 5 (continued…)

	Ga		As		Rb		Sr		Zr		Mo		Ag	
Sample Name	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit
0	98.34	ng/l	95.53	ng/l	34.65	ng/l	429.4	ng/l	<2.12	ng/l	124.3	ng/l	2.76	ng/l
10ppb	9.90	ug/l	9.90	ug/l	9.97	ug/l	9.57	ug/l	10.30	ug/l	9.29	ug/l	10.00	ug/l
Site A	433.09	ug/l	15.28	ug/l	4.48	mg/l	3.93	mg/l	281.0	ng/l	1.56	ug/l	4.00	ug/l
Site B	267.43	ug/l	18.47	ug/l	4.95	mg/l	4.09	mg/l	126.1	ng/l	1.46	ug/l	1.43	ug/l
Site C	327.56	ug/l	32.64	ug/l	5.84	mg/l	3.23	mg/l	271.3	ng/l	2.73	ug/l	1.71	ug/l
Site D	272.52	ug/l	18.36	ug/l	4.89	mg/l	4.03	mg/l	47.81	ng/l	1.38	ug/l	1.71	ug/l
Site E	779.93	ug/l	2.20	ug/l	3.66	mg/l	3.70	mg/l	24.54	ng/l	249.7	ng/l	2.85	ug/l
Site F	453.71	ug/l	16.31	ug/l	4.89	mg/l	4.16	mg/l	30.04	ng/l	1.55	ug/l	1.43	ug/l
Site G	601.00	ug/l	2.77	ug/l	2.10	mg/l	3.84	mg/l	14.81	ng/l	72.35	ng/l	3.43	ug/l
Site H	594.66	ug/l	2.60	ug/l	2.21	mg/l	3.71	mg/l	10.15	ng/l	62.16	ng/l	<1.42	ug/l
Site A, total acid soluble (aa)	744.01	ug/l	18.69	ug/l	4.73	mg/l	4.04	mg/l	20.73	ng/l	1.25	ug/l	1.43	ug/l
Site B (aa)	671.64	ug/l	25.18	ug/l	5.08	mg/l	4.22	mg/l	33.42	ng/l	1.34	ug/l	<1.42	ug/l
Site C (aa)	1.09	mg/	49.69	ug/l	6.67	mg/l	4.02	mg/l	376.3	ng/l	2.38	ug/l	2.85	ug/l
Site D (aa)	648.89	ug/l	18.81	ug/l	4.84	mg/l	4.14	mg/l	28.35	ng/l	1.27	ug/l	<1.42	ug/l
Site E (aa)	1.02	mg/	3.91	ug/l	3.37	mg/l	4.16	mg/l	74.04	ng/l	200.7	ng/l	<1.42	ug/l
Site F (aa)	510.65	ug/l	18.04	ug/l	4.74	mg/l	4.30	mg/l	37.65	ng/l	1.38	ug/l	1.43	ug/l
Site G (aa)	760.99	ug/l	3.29	ug/l	2.12	mg/l	3.94	mg/l	13.11	ng/l	68.27	ng/l	<1.42	ug/l
Site H (aa)	594.53	ug/l	3.15	ug/l	1.75	mg/l	3.57	mg/l	8.88	ng/l	-39.75	ng/l	<1.42	ug/l
blank	14.47	ug/l	79.92	ng/l	53.79	ug/l	67.89	ug/l	3.38	ng/l	-100.89	ng/l	13.43	ug/l

	Cd		Sb		Ba		Ta		W		Tl		Pb	
Sample Name	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit	Conc.	SQ Unit
0	22.11	ng/l	101.27	ng/l	525.00	ng/l	3.89	ng/l	9.22	ng/l	5.40	ng/l	99.15	ng/l
10ppb	9.98	ug/l	12.09	ug/l	9.48	ug/l	26.58	ug/l	29.33	ug/l	9.99	ug/l	9.90	ug/l
Site A	62.24	ng/l	208.39	ng/l	492.76	ug/l	197.34	ng/l	573.14	ng/l	10.28	ug/l	-0.63	ng/l
Site B	70.09	ng/l	63.66	ng/l	296.38	ug/l	132.32	ng/l	603.40	ng/l	7.99	ug/l	14.25	ng/l
Site C	21.04	ng/l	181.37	ng/l	361.71	ug/l	111.28	ng/l	1.25	ug/l	8.85	ug/l	-21.49	ng/l
Site D	-0.53	ng/l	6.75	ng/l	287.77	ug/l	62.95	ng/l	536.79	ng/l	6.28	ug/l	-31.72	ng/l
Site E	1.43	ng/l	12.53	ng/l	885.14	ug/l	53.13	ng/l	92.44	ng/l	7.71	ug/l	45.71	ng/l
Site F	-12.30	ng/l	-7.72	ng/l	502.74	ug/l	43.58	ng/l	318.80	ng/l	7.71	ug/l	-56.18	ng/l
Site G	3.39	ng/l	-19.30	ng/l	689.16	ug/l	26.66	ng/l	25.87	ng/l	6.85	ug/l	-59.94	ng/l
Site H	-8.38	ng/l	33.75	ng/l	657.77	ug/l	22.57	ng/l	34.35	ng/l	4.85	ug/l	-77.93	ng/l
Site A, total acid soluble (aa)	-2.50	ng/l	-3.86	ng/l	877.37	ug/l	20.66	ng/l	85.25	ug/l	4.57	ug/l	152.58	ng/l
Site B (aa)	3.39	ng/l	10.60	ng/l	739.41	ug/l	19.29	ng/l	358.94	ug/l	5.42	ug/l	229.05	ng/l
Site C (aa)	44.58	ng/l	155.31	ng/l	1.23	mg/l	34.03	ng/l	6.17	ug/l	18.57	ug/l	2.66	ug/l
Site D (aa)	1.43	ng/l	2.89	ng/l	748.98	ug/l	11.65	ng/l	200.67	ug/l	4.57	ug/l	194.18	ng/l
Site E (aa)	-2.50	ng/l	-45.34	ng/l	1.13	mg/l	10.84	ng/l	4.02	ug/l	8.85	ug/l	1.00	ug/l
Site F (aa)	-8.38	ng/l	10.61	ng/l	593.40	ug/l	16.02	ng/l	2.50	ug/l	3.42	ug/l	597.23	ng/l
Site G (aa)	-8.38	ng/l	-21.22	ng/l	814.88	ug/l	10.84	ng/l	1.45	ug/l	5.71	ug/l	191.33	ng/l
Site H (aa)	-6.42	ng/l	-27.98	ng/l	690.51	ug/l	8.38	ng/l	934.49	ng/l	1.99	ug/l	156.07	ng/l
blank	395.80	ng/l	-91.63	ng/l	15.67	ug/l	8.65	ng/l	690.93	ng/l	<1.43	ug/l	-75.47	ng/l

Appendix 6: Raw data from the quantitative scan of dry season samples for HNO_3 acid soluble elements

	A	B	C	D	E	F	G	H	HUdup	BLANK
	µg/L	µg/L	µg/L		µg/L			µg/L	µg/L	µg/L
Li	2050.00	2080.00	2150.00		93.70			3.28	3.14	0.46
Na	52300.00	50300.00	66300.00		11700.00			5930.00	5950.00	25.20
Mg	11900.00	11900.00	20300.00		9650.00			6440.00	6470.00	0.92
Al	8.58	2.83	41.40		13.20			175.00	178.00	<DL
Si	6190.00	6980.00	5980.00		2760.00			2010.00	2000.00	88.30
K	10300.00	10700.00	7060.00		13100.00			12500.00	12900.00	14.60
Ca	3860.00	4130.00	2370.00		3440.00			2990.00	3150.00	0.70
V	<DL	<DL	2.08		<DL			1.12	1.16	<DL
Cr	0.04	0.07	0.27		0.07			0.12	0.11	<DL
Mn	206.00	66.30	101.00		288.00			1050.00	1070.00	0.06
Fe	159.00	38.10	140.00		194.00			813.00	819.00	<DL
Co	0.36	0.11	0.30		0.36			2.35	2.38	<DL
Ni	0.32	0.29	1.11		0.76			1.34	1.38	<DL
Cu	0.96	0.63	3.28		0.98			3.50	3.51	<DL
Zn	1.34	0.95	1.95		1.37			5.47	5.70	<DL
As	13.50	16.80	35.70		2.20			3.54	3.58	<DL
Sr	136.00	148.00	87.70		126.00			103.00	104.00	0.01
Ru	<DL	<DL	<DL		<DL			<DL	<DL	<DL
Cd	0.01	<DL	0.02		0.01			0.03	0.03	0.03
Sn	<DL	<DL	<DL		<DL			<DL	<DL	<DL
Sb	<DL	<DL	0.03		<DL			<DL	<DL	<DL
Cs	0.04	0.08	0.27		0.02			0.04	0.04	<DL
Ta	0.10	0.09	0.10		0.08			0.07	0.06	0.03
W	0.10	0.10	0.32		0.03			0.02	0.02	<DL
Pb	0.15	0.17	0.43		0.34			4.04	4.06	<DL

Appendix 7: Raw data from the quantitative scan of dry season samples for dissolved elements

	A	B	C	D	E	F	G	H
	µg/L	µg/L	µg/L		µg/L			µg/L
Li	416.00	371.00	2100.00		102.00			42.10
Na	10600.00	9020.00	68500.00		4600.00			2330.00
Mg	2650.00	2440.00	19900.00		2540.00			1650.00
Al	1.34	0.94	6.81		1.18			1.56
Si	4950.00	4910.00	5580.00		2420.00			704.00
K	1980.00	1790.00	7460.00		2870.00			2340.00
Ca	1700.00	1540.00	2300.00		1340.00			719.00
V	<DL	<DL	2.72		<DL			<DL
Cr	<DL	<DL	0.17		0.01			0.06
Mn	46.70	3.46	0.63		0.41			71.60
Fe	2.80	0.96	21.90		1.30			5.59
Co	0.14	0.05	0.30		0.09			0.30
Ni	0.22	0.20	1.11		0.47			0.77
Cu	0.83	0.55	2.43		1.06			1.13
Zn	1.22	1.59	1.40		1.03			2.12
As	3.64	3.68	36.70		1.02			1.25
Sr	58.90	54.20	87.50		48.10			22.60
Ru	<DL	<DL	<DL		<DL			<DL
Cd	0.10	0.01	0.01		0.01			0.03
Sn	<DL	<DL	<DL		<DL			<DL
Sb	<DL	<DL	0.03		<DL			<DL
Cs	0.03	0.03	0.20		0.01			0.02
Ta	0.27	0.18	0.21		0.12			0.10
W	0.10	0.08	0.56		0.06			0.04
Pb	0.01	0.01	0.24		0.01			0.01